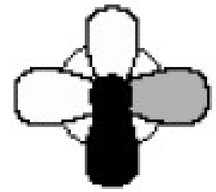
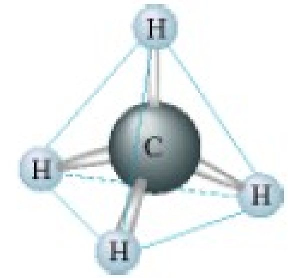
OLED

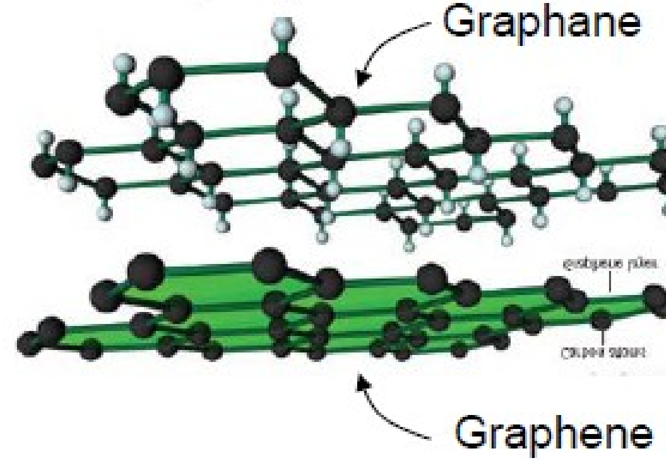
MOLTEPLICITA' di LEGAMI nel CARBONIO

Ibridizza: sp^3

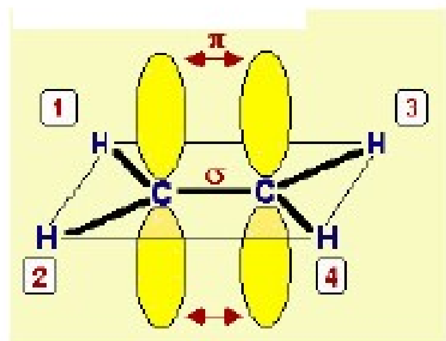




Diamante,
Metano (CH_4)

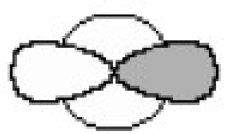


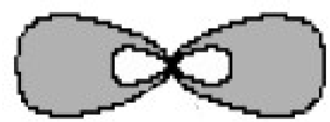
sp^2



etilene

sp

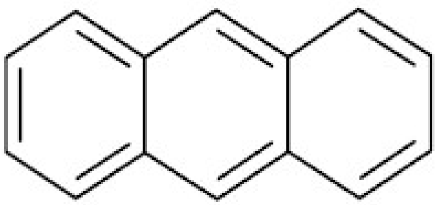


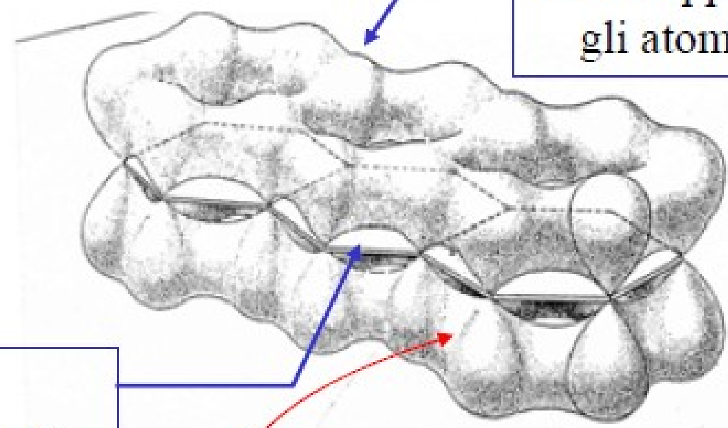


Si può quindi legare con altri atomi di carbonio in <u>strutture planari</u>
con legami σ (forti) nel piano e legami π fuori dal piano

MOLECOLE π-CONIUGATE

Elettroni del LUMO, liberi di muoversi lungo la molecola sfruttando la sovrapposizione degli orbitali p_z con gli atomi vicini (delocalizzazione)

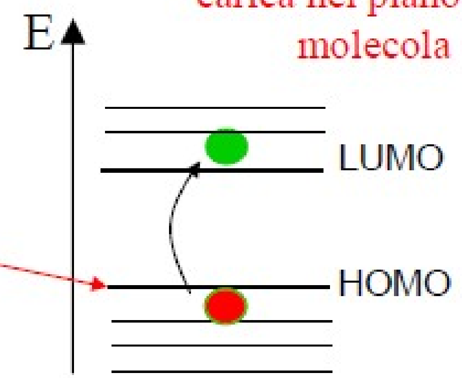




antracene

Elettroni fortemente localizzati tra i nuclei dei C partecipanti al legame σ

"Facile" CONDUZIONE di carica nel piano della molecola



Gli elettroni degli orbitali p_z (elettroni π) sono a più alta energia (HOMO – Highest Occupied Molecular Orbital)

Dati i deboli legami π, gli elettroni π sono i più facilmente eccitabili al livello superiore (LUMO – Lowest Unoccupied …)

MOLECOLE e BANDE !!!

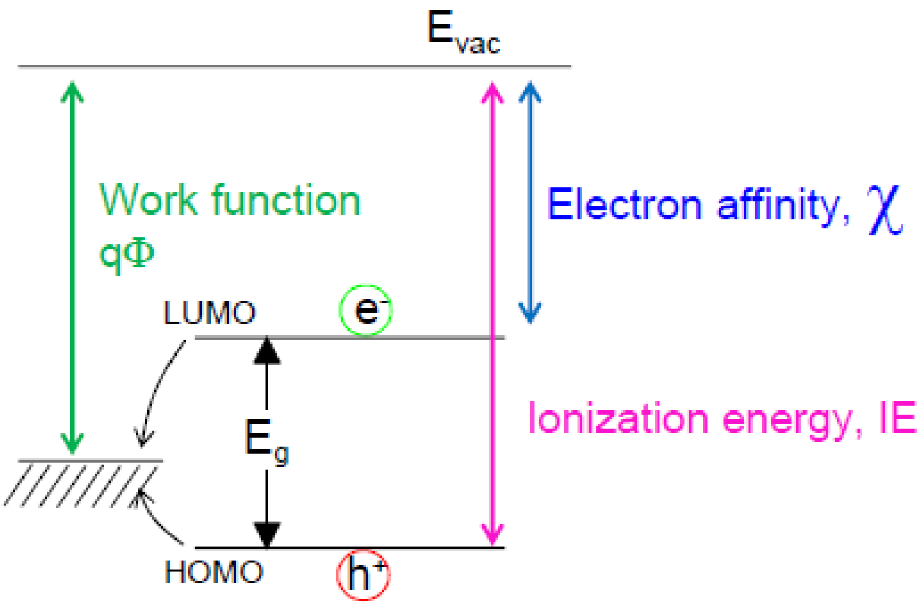
Molecola $\rightarrow$ livelli energetici molecolari

originati dagli atomi (in numero finito) della molecola

In analogia con i cristalli inorganici e per semplicità di analisi, i semiconduttori organici possono anch'essi essere rappresentati da:

- livelli energetici (banda di valenza e di conduzione) separati da un gap energetico

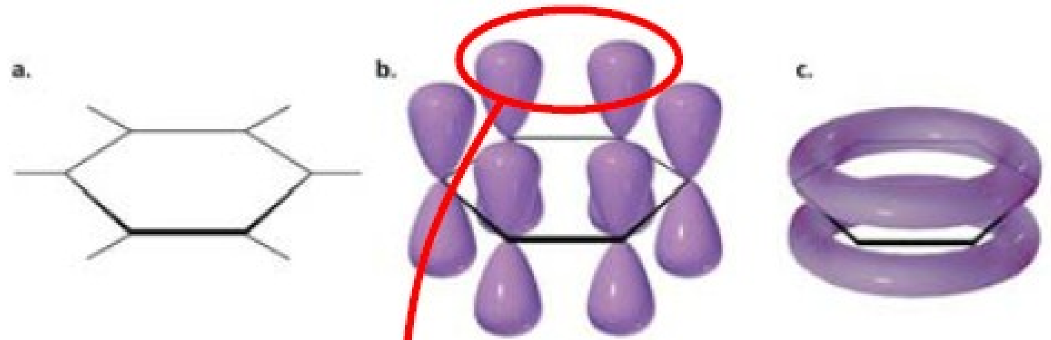
- 2 portatori di carica, elettroni e lacune



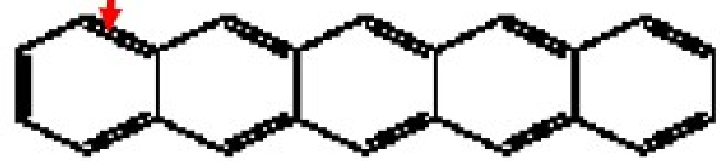
Per la maggior parte dei materiali coniugati <u>il "gap" è nel visibile</u>

PRINCIPALI MOLECOLE π-CONIUGATE

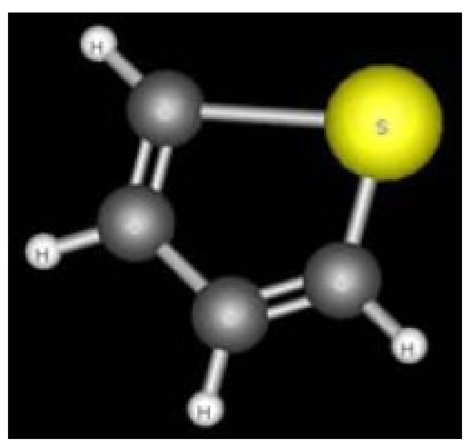
Anello benzenico
C_6H_6



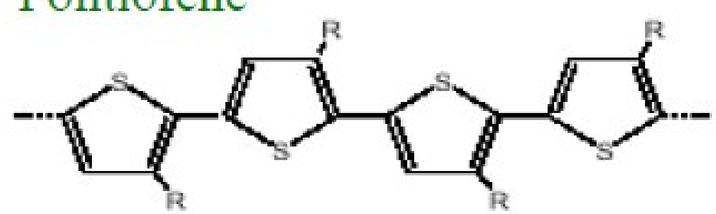
Pentacene



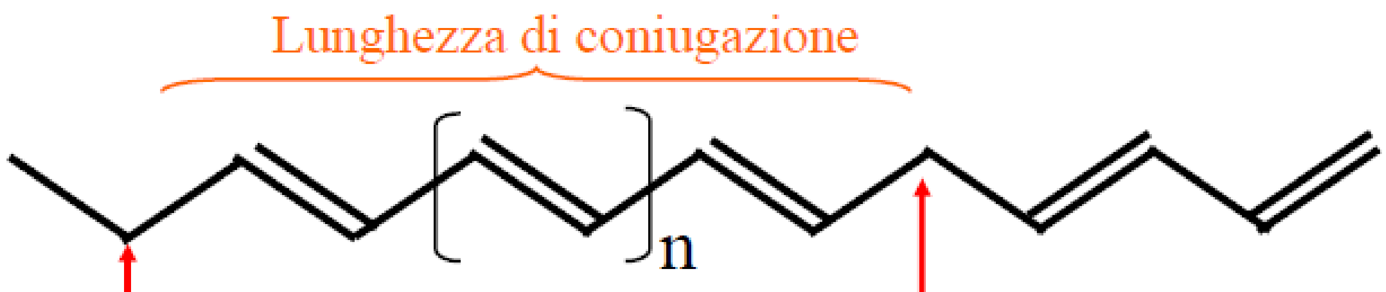
Anello tiofenico
SC_4H_4



Politiofene



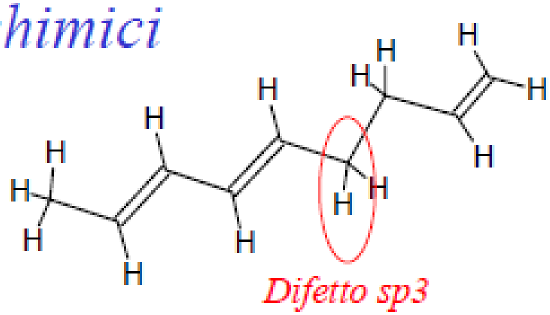
LUNGHEZZA di CONIUGAZIONE



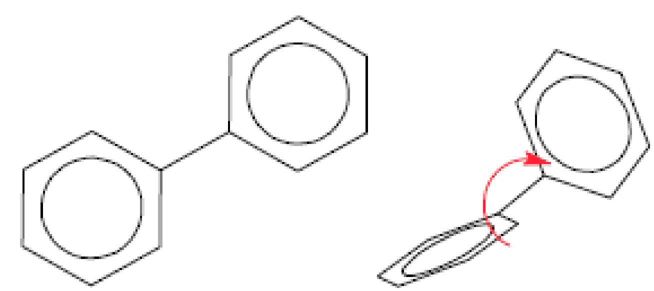
Poliacetilene

La coniugazione (e quindi la **<u>CONDUCIBILITA'</u>**) lungo la catena può essere diminuita a causa di:

difetti chimici



effetti conformazionali



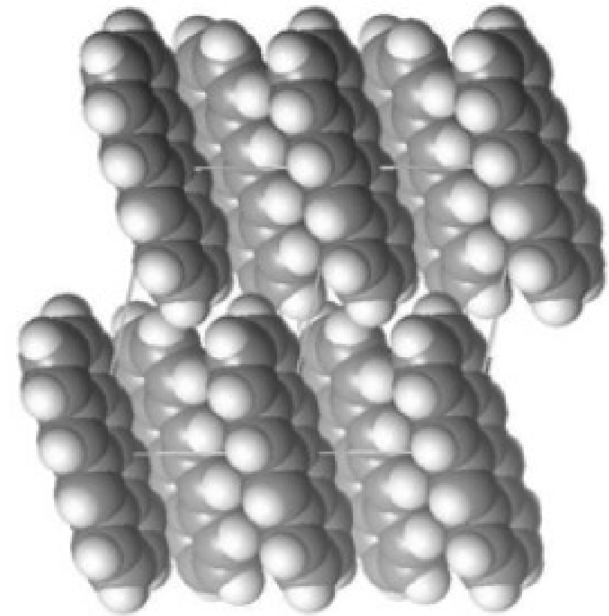
ORGANIZZAZIONE SPAZIALE

Molecole organizzate nello spazio :

cristallo molecolare

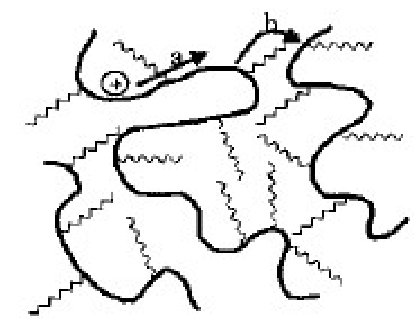
forte sovrapposizione degli orbitali p_z

delocalizzazione dell'elettrone su "tutto il cristallo"

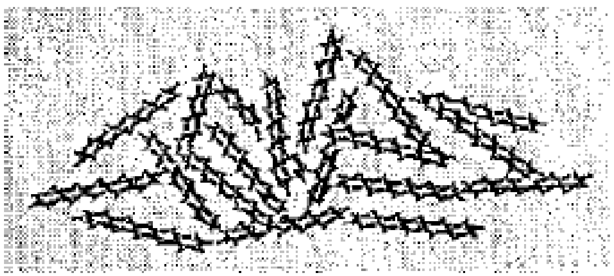


Film amorfo

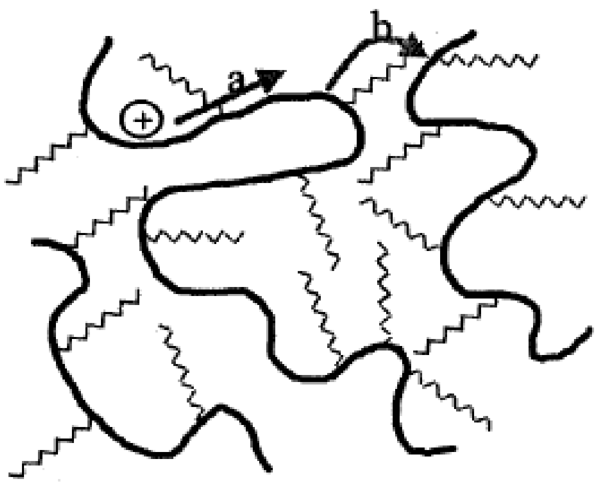
Le molecole sono legate da forze di Van der Wals (deboli)



IL TRASPORTO DELLA CARICA
film amorfo



a- trasporto della carica lungo la molecola (o il polimero) - *facile*

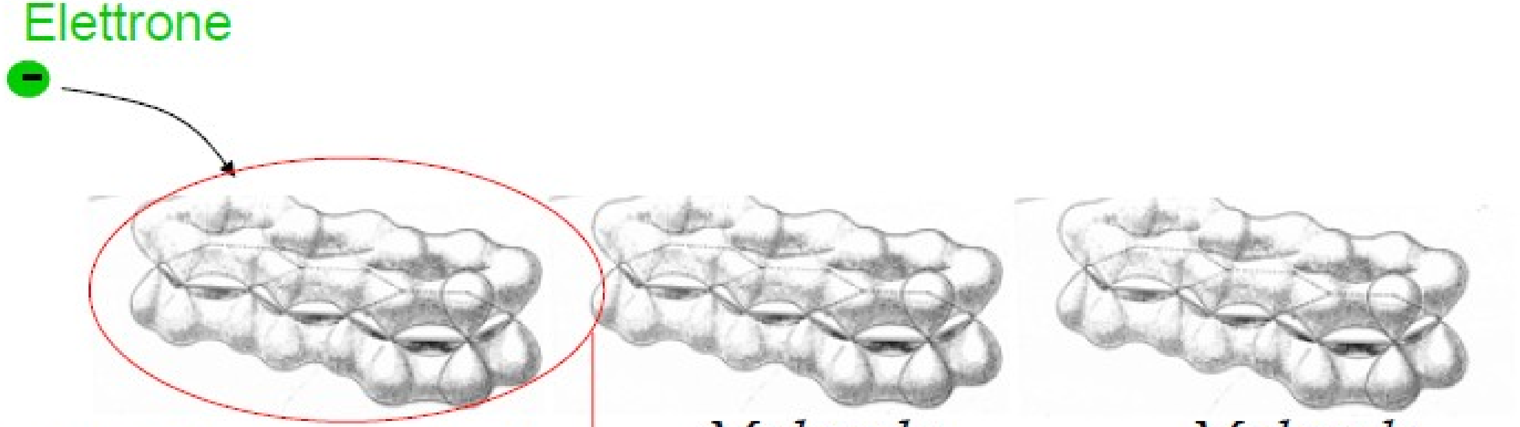


b- trasporto della carica da una molecola all'altra - *difficile*
Fenomeno reso ancora più complicato dal fatto che la distanza tra le catene ha una distribuzione casuale

→ Variable range hopping
emissione termoionica o tunneling

→ Bassa mobilità dei portatori, dettata dal fenomeno più lento.

CONDIZIONI per il TRASPORTO



Molecola che si "carica" negativamente (<u>Riduzione</u>)

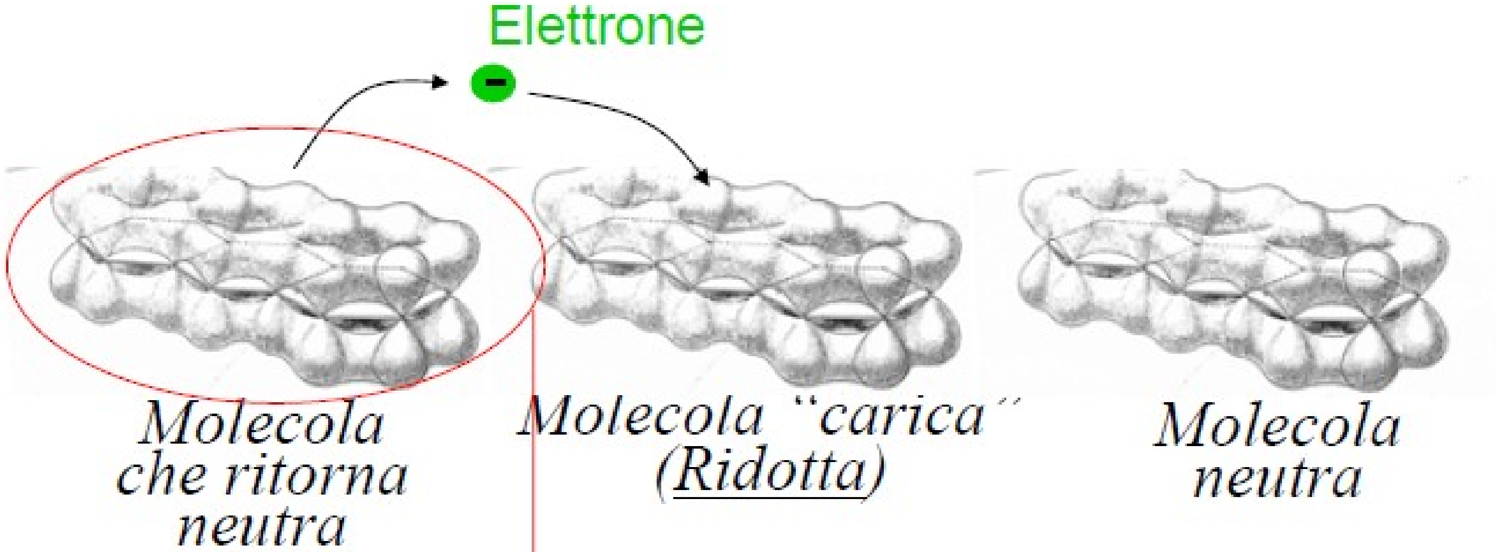
Molecola neutra

Molecola neutra

Viene chiamata anche
POLARONE
perché viene modificata la distribuzione di carica su di essa

La molecola ridotta non deve reagire chimicamente o modificarsi strutturalmente

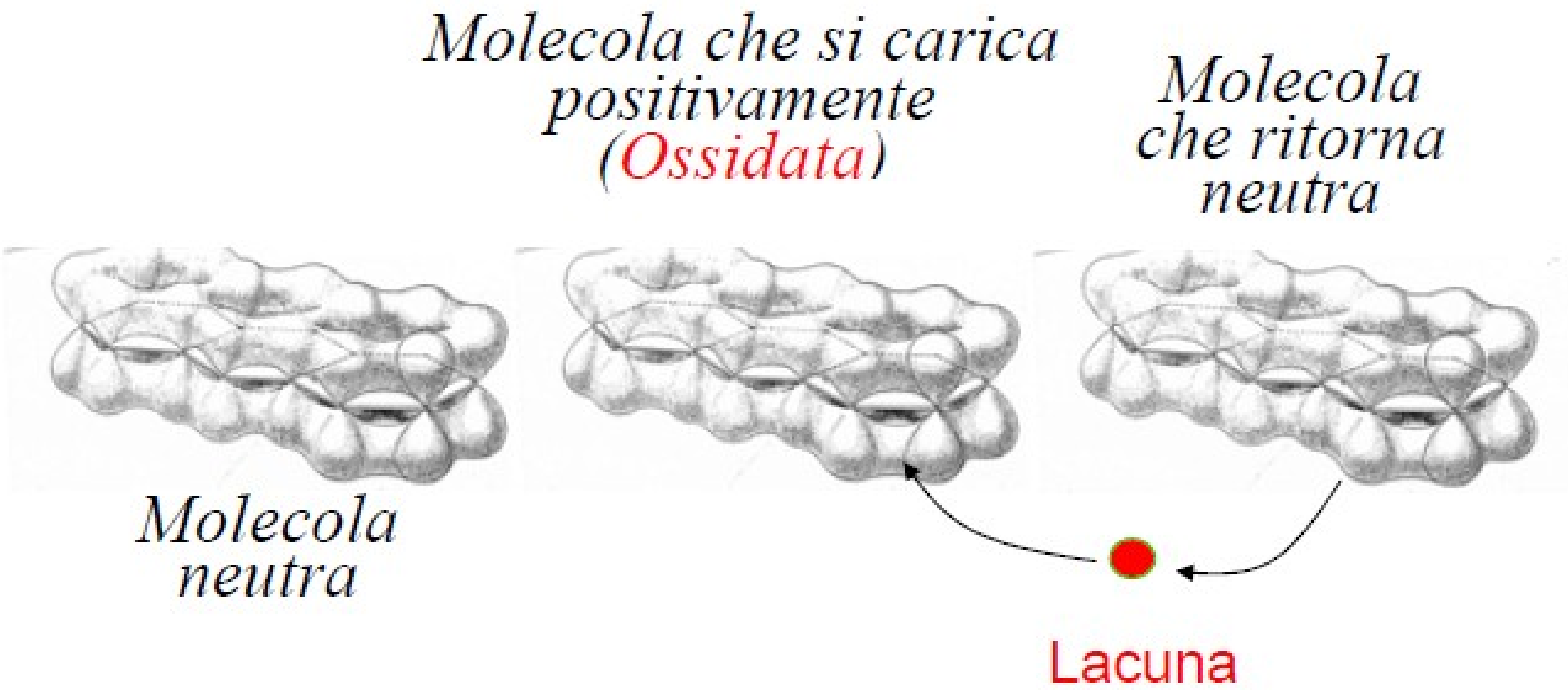
CONDIZIONI per il TRASPORTO



La molecola deve ritornare <u>esattamente</u> nello stato iniziale

RIDUZIONE REVERSIBILE

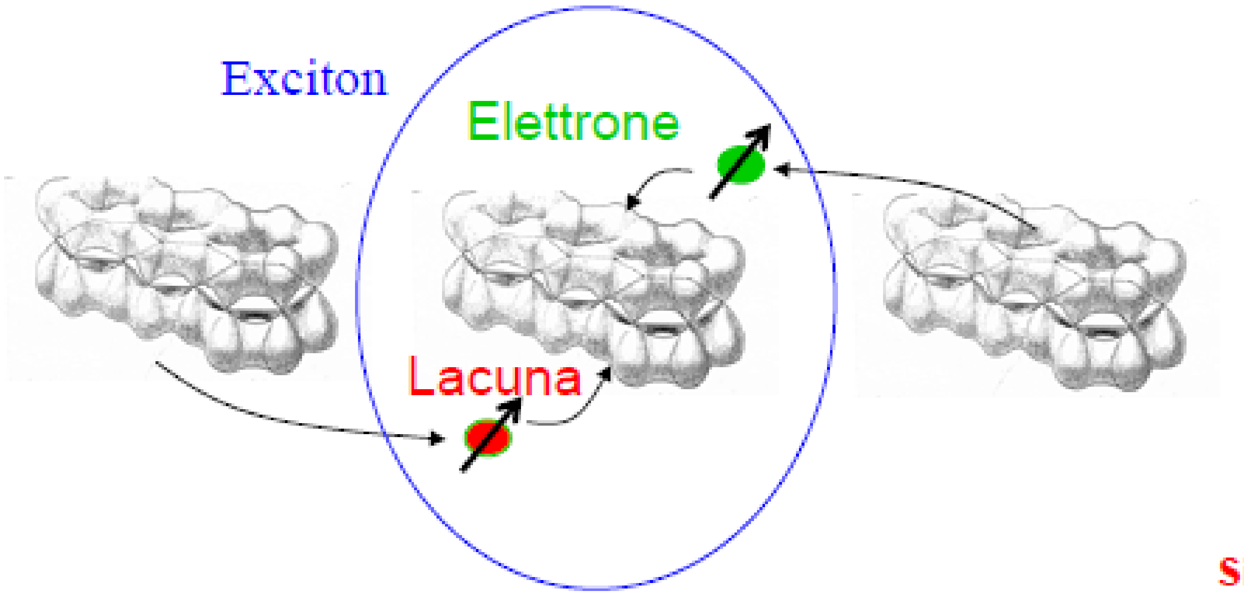
CONDIZIONI per il TRASPORTO



Le molecole di interesse per i dispositivi devono sostenere

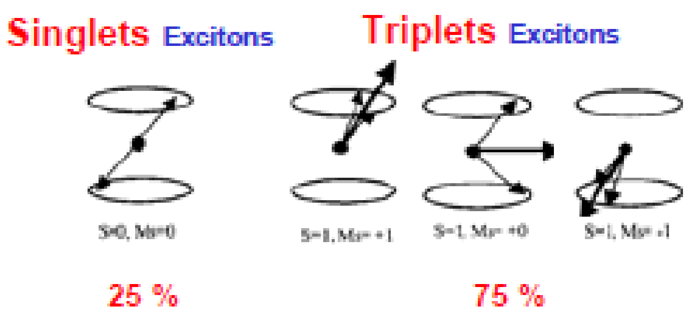
OSSIDO-RIDUZIONI REVERSIBILI

RICOMBINAZIONE DI CARICA



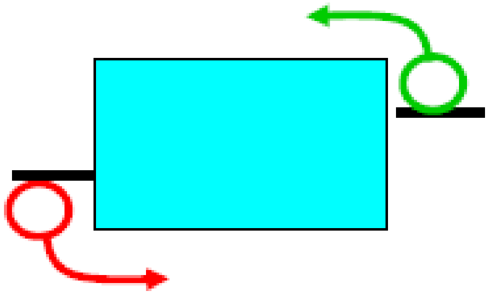
e^- and h^+ have spin

Spin momentum
should be conserved
for radiative decay

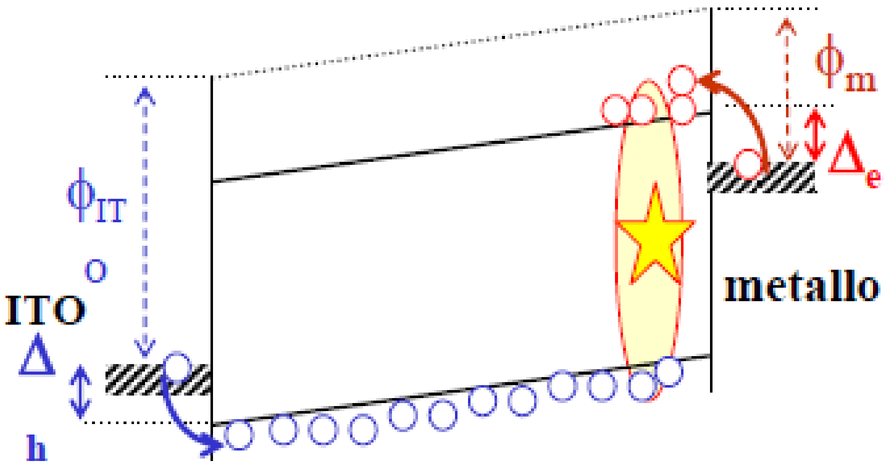


$$\eta_{ext} = \gamma \cdot r_{st} \cdot r_{EL} \cdot \eta_{coupling}$$

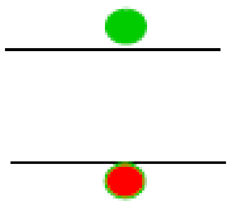
RICOMBINAZIONE RADIATIVA



I due contatti metallo-semiconduttore sono importanti !



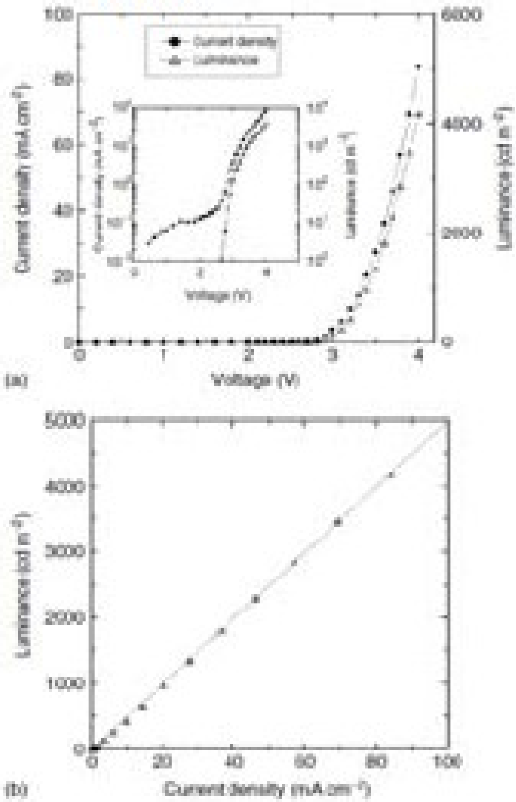
1. Iniezione controllata di entrambi i portatori
2. Trasporto
3. Formazione dell'eccitone
4. Ricombinazione con emissione di un fotone *(ricombinazione radiativa nel visibile)*



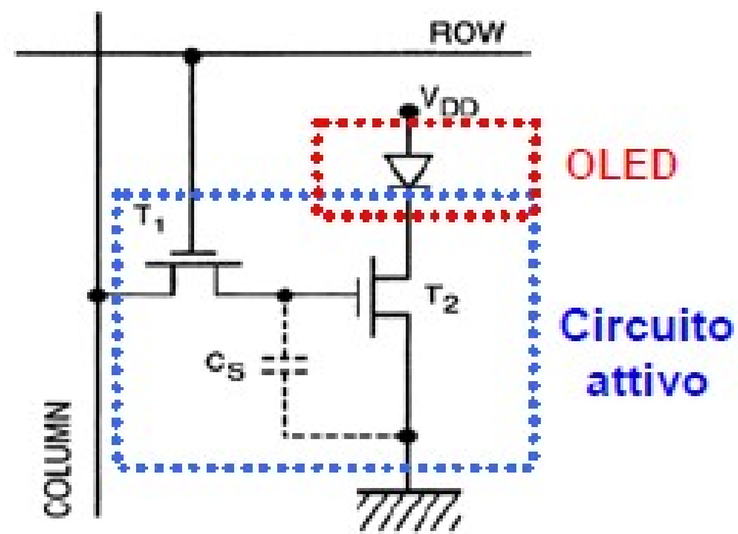
OLED

CARATTERISTICHE di un OLED

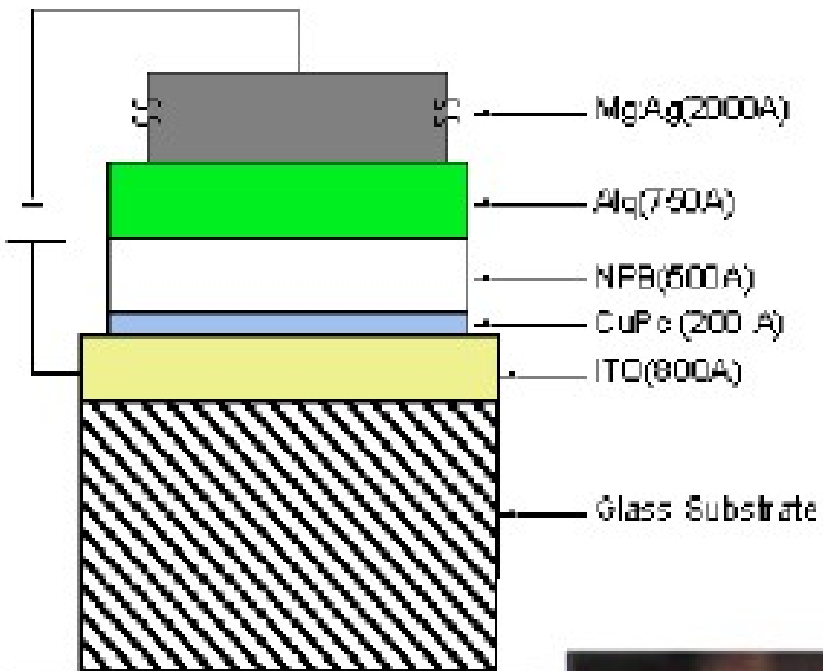
Collaborazione TESEO



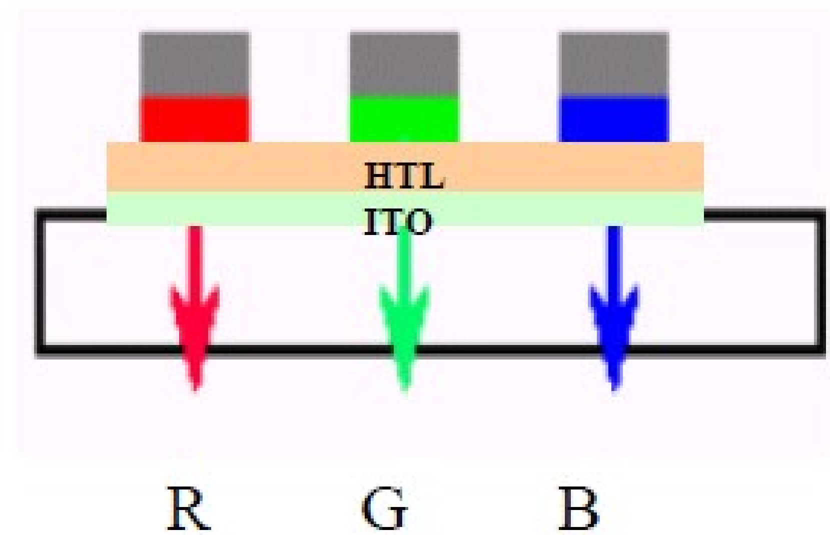
- Pilotaggio di ogni oLED in corrente
- Memorizzazione della corrente

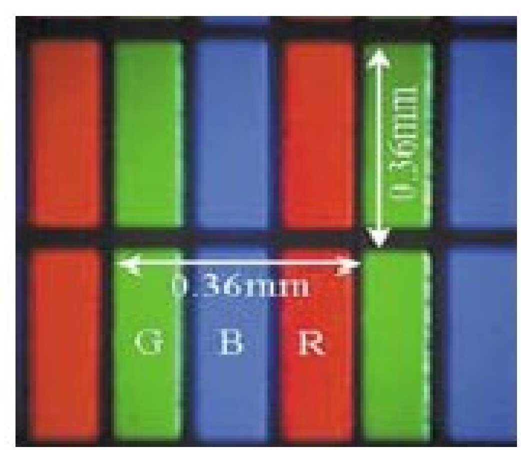


Da OLED a PIXEL

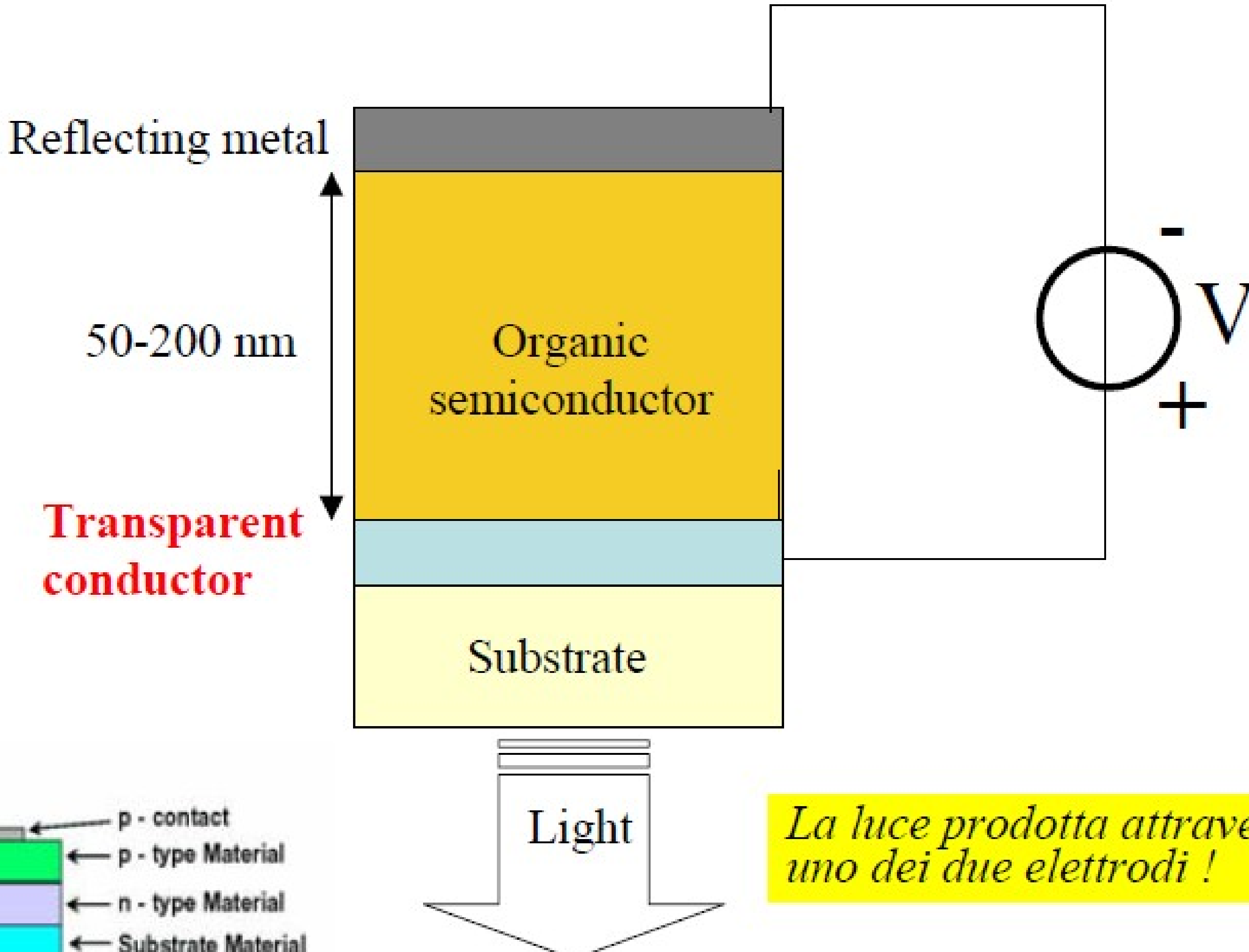


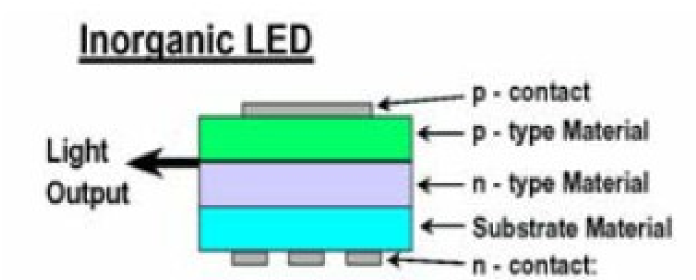
MOLECOLE SEMPLICI





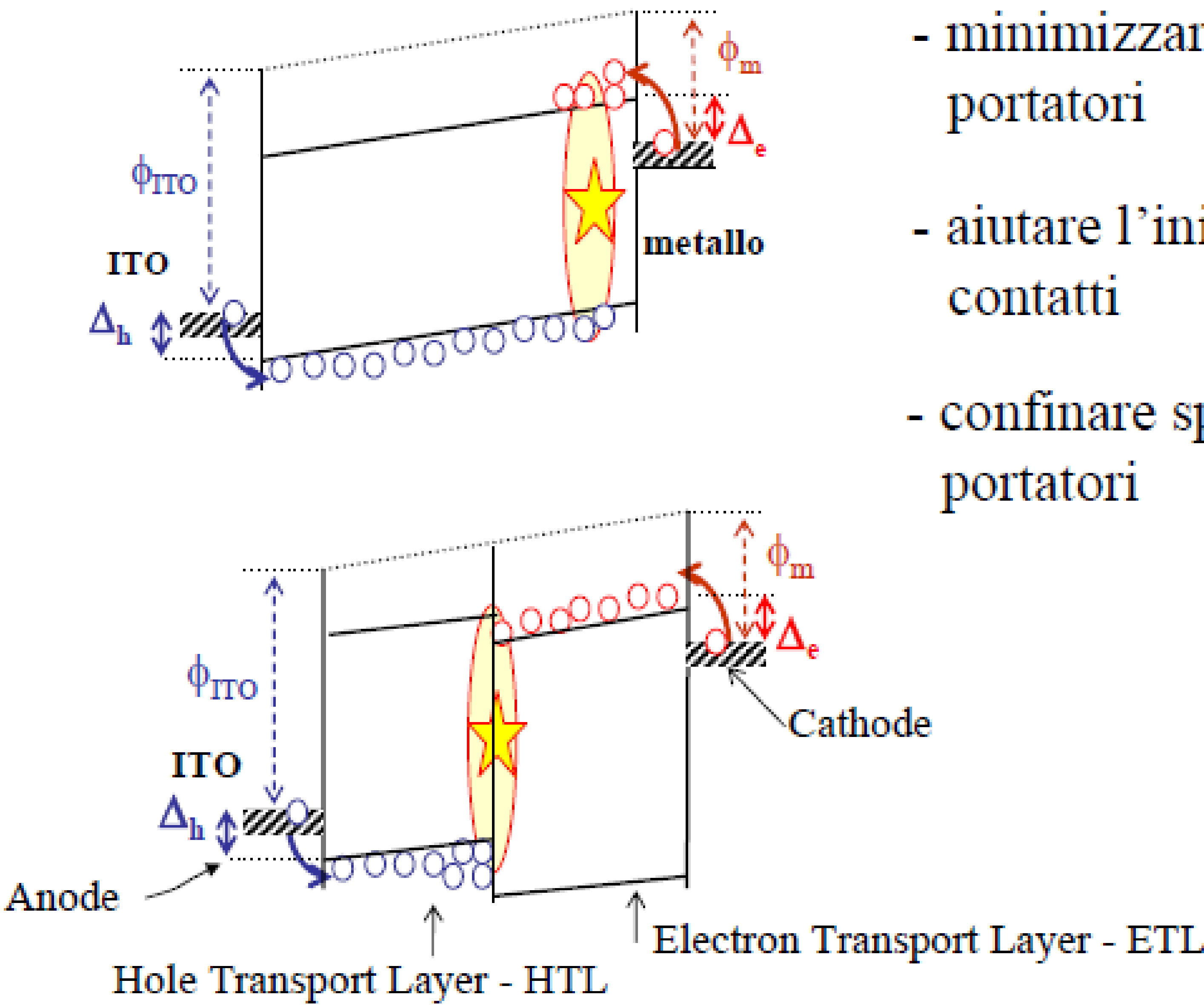
ORGANIC LED





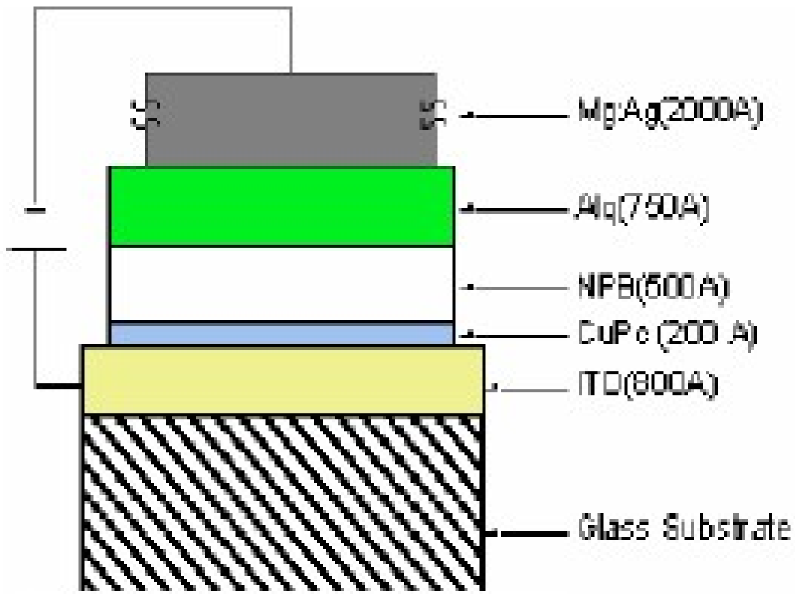
La luce prodotta attraversa uno dei due elettrodi !

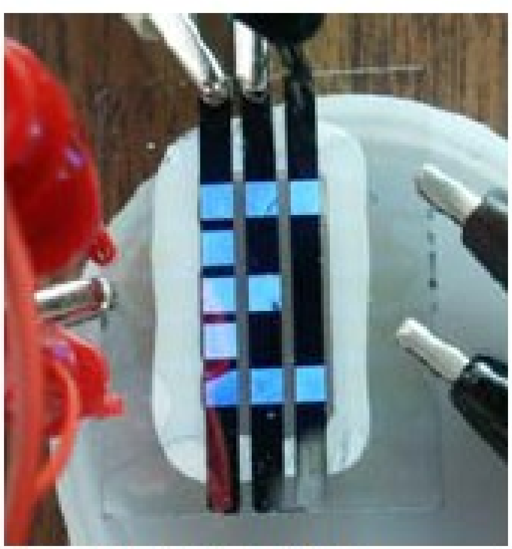
RICOMBINAZIONE RADIATIVA



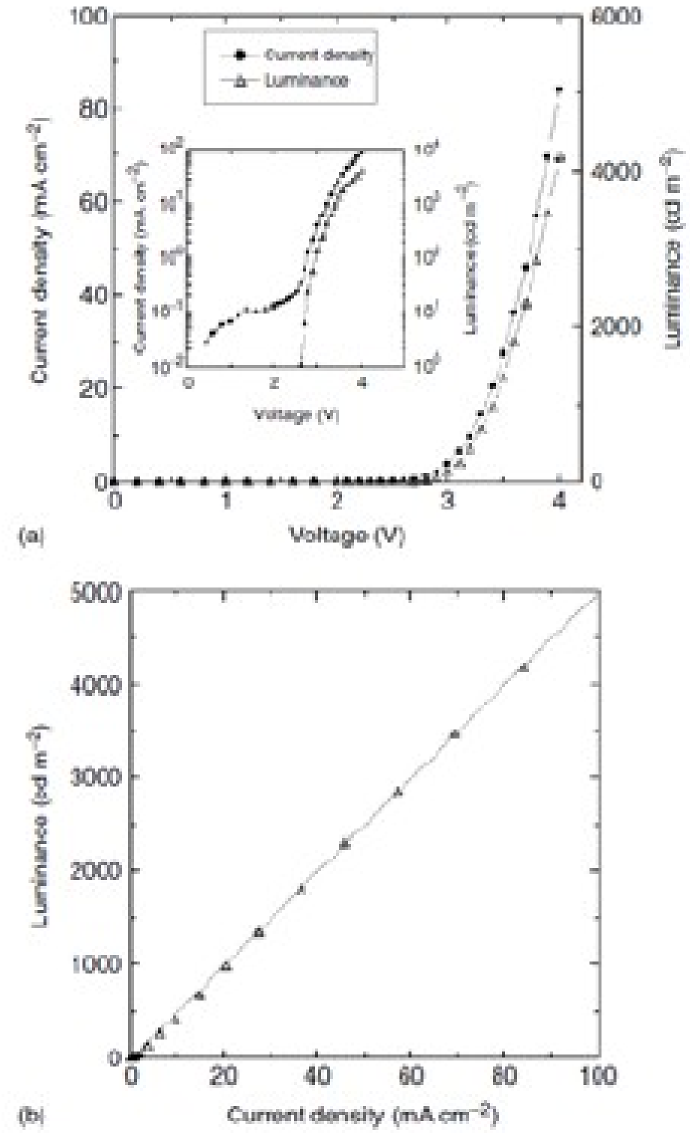
- minimizzare la corrente di portatori
- aiutare l'iniezione dai contatti
- confinare spazialmente i portatori

CARATTERISTICHE di un OLED





Collaborazione TESEO



Typical I-V-L characteristics of OLED

ELETTROLUMINESCENCE EFFICIENCY

Loss mechanisms
(limiting devices efficiency):

- Charge un-balance (γ)
- Singlets vs Triplets (r_{st})
- Intrinsic material efficiency (η_{pl})
- Light extraction ($\eta_{coupling}$)

These factors can be combined to define the external quantum efficiency as:

$$\boxed{\eta_{ext} = \gamma \cdot r_{st} \cdot \eta_{PL} \cdot \eta_{coupling}}$$

$$\boxed{\frac{\text{n. fotoni emessi}}{\text{n. cariche iniettate}}}$$

BILANCIAMENTO DELLA CARICA (I)

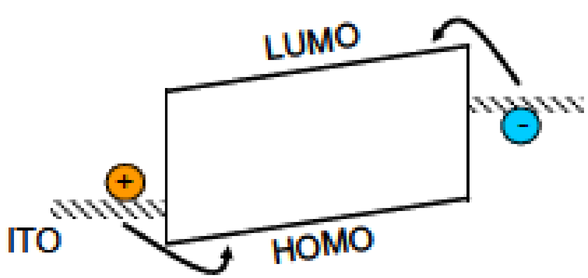
$$\eta_{ext} = \gamma \cdot r_{st} \cdot \eta_{PL} \cdot \eta_{coupling}$$

Probability that e^-&h^+ meet and form excitons

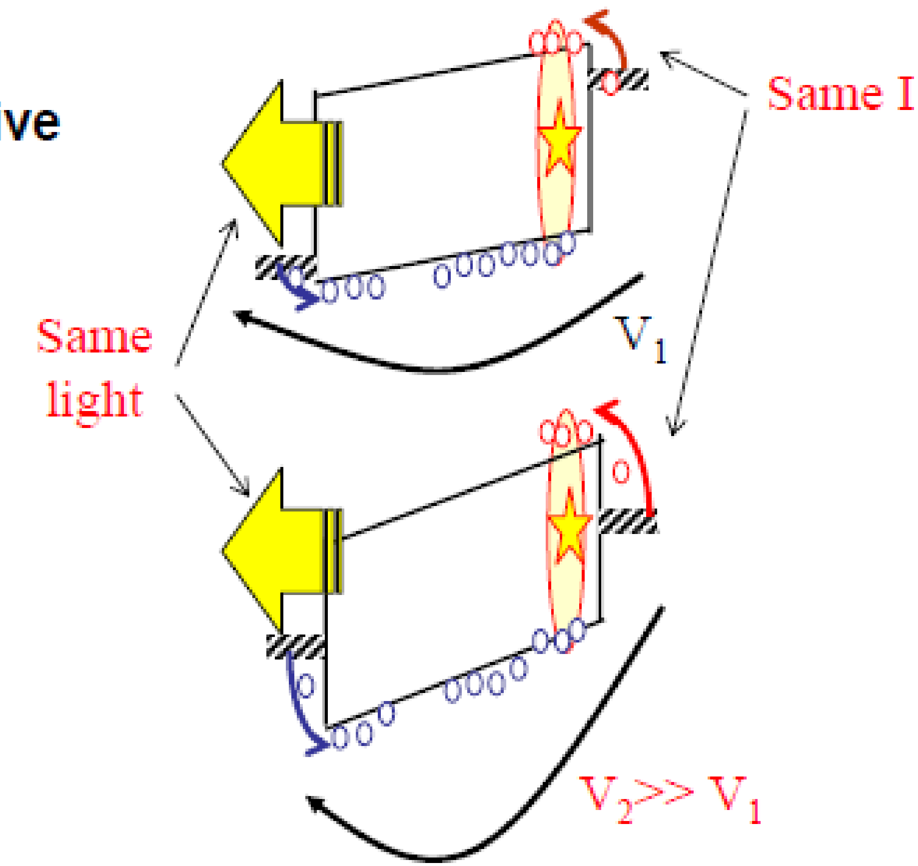
Small barriers increase power efficiency

$$P_{eff} \div \eta_{ext} \cdot \frac{h\nu}{eV}$$

Balance of positive and negative carriers injected



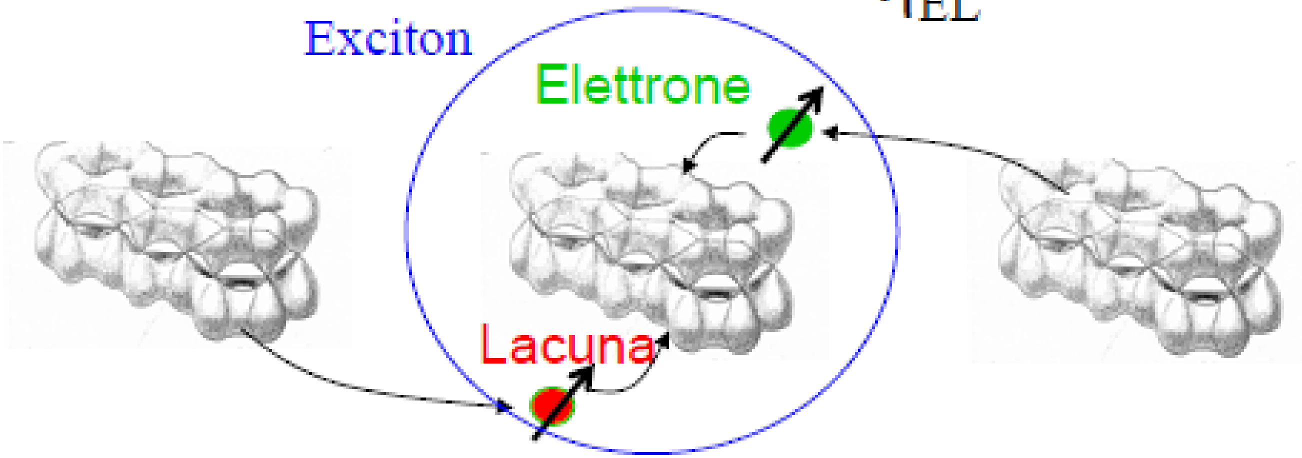
Carrier injection



Equivalent barriers for holes and electrons is beneficial

SINGLET - TRIPLET RATIO

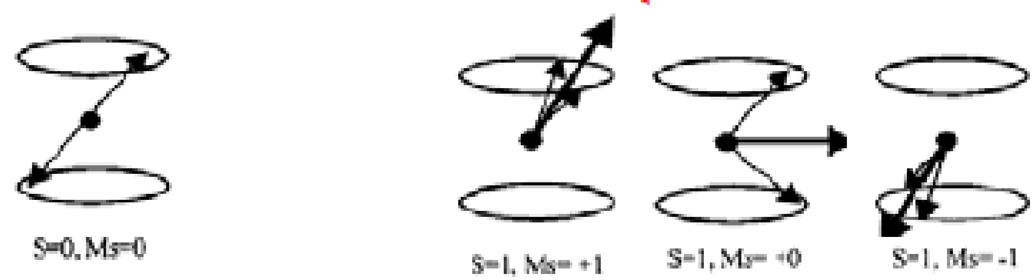
$$\eta_{ext} = \gamma \cdot \underbrace{r_{st} \cdot r_{EL}}_{\eta_{EL}} \cdot \eta_{coupling}$$



e^- and h^+ have spin.

Capture of e^- and h^+ (Exciton formation) is spin-independent.

Singlets Excitons **Triplets Excitons**

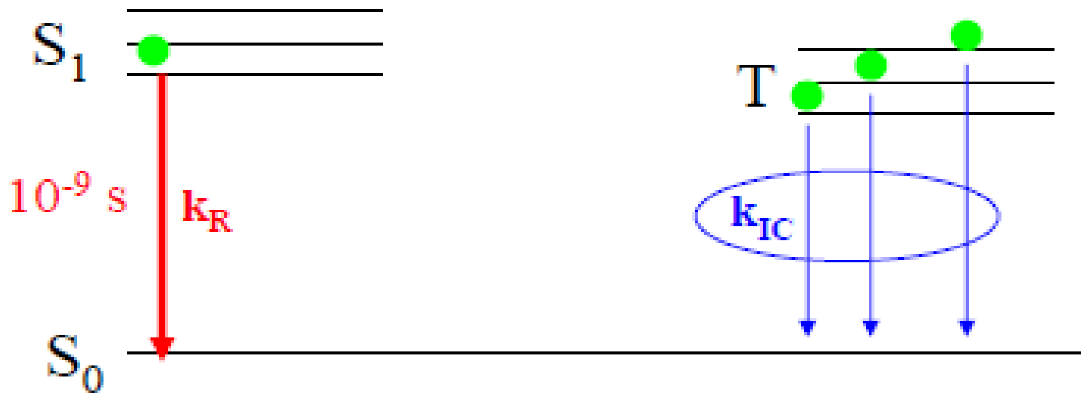


25 % **75 %**

FLUORESCENCE

25%
Excitons with
SINGLET character …

75%
Excitons with TRIPLET
character



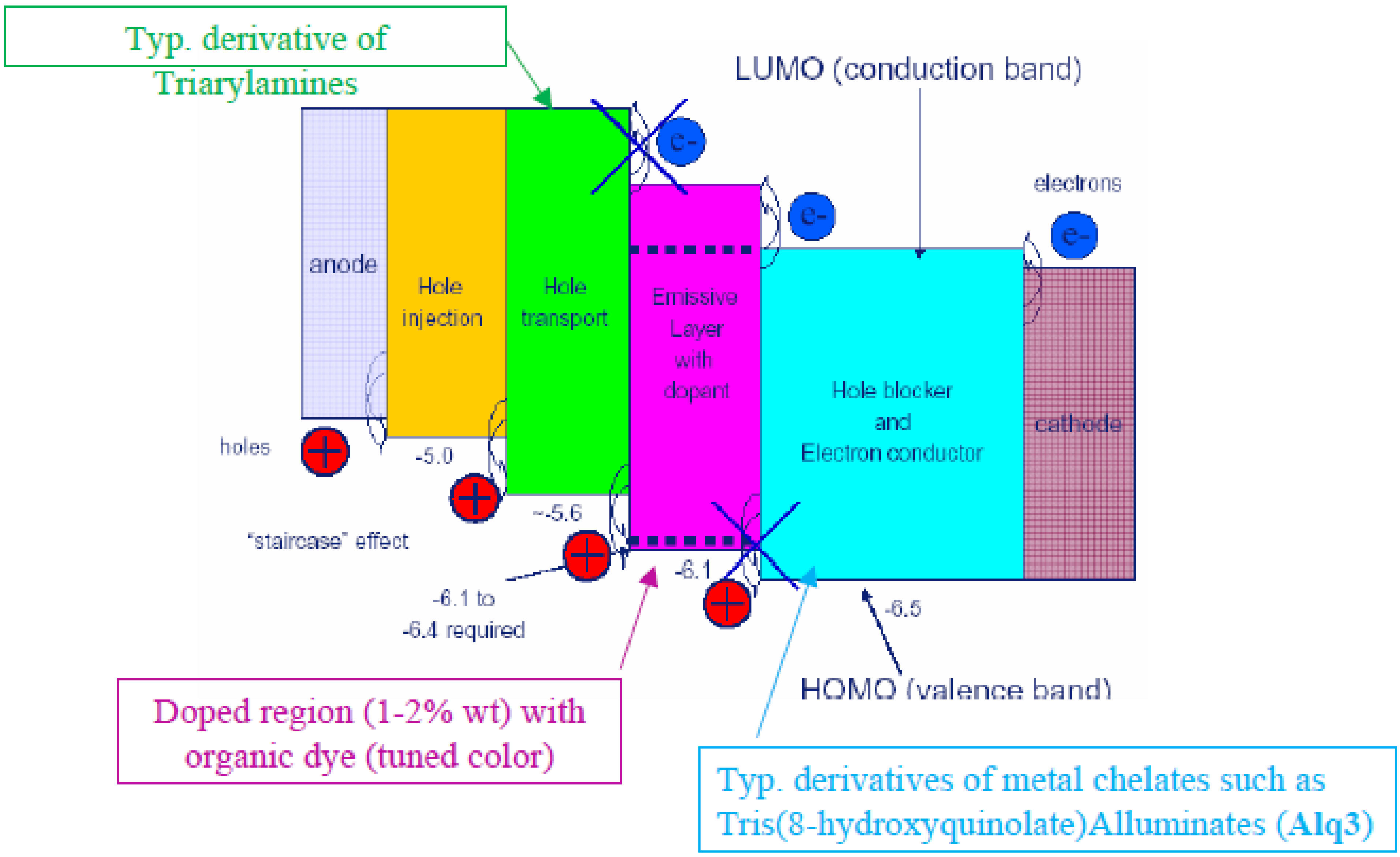
k = rate di decadimento.
Tempo di vita misurato =1/k

… undergo radiative recombination FLUORESCENCE

NON radiative recombination

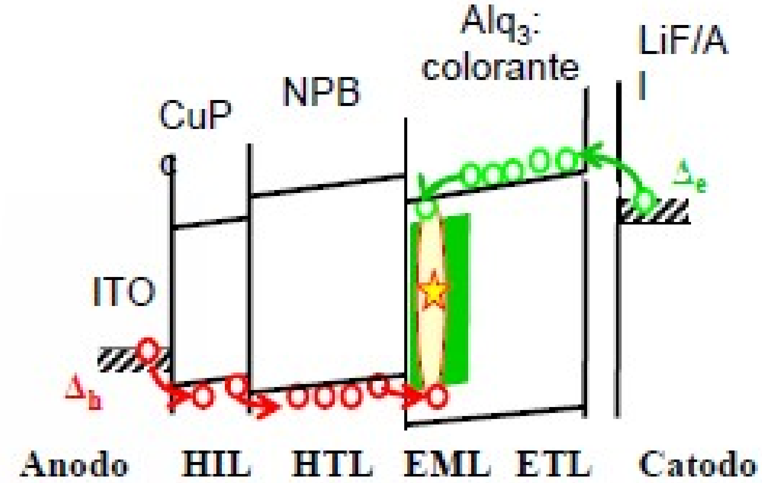
In conventional fluorescent devices only singlet excitons (25%) recombine radiatively (75% goes into heat) at best

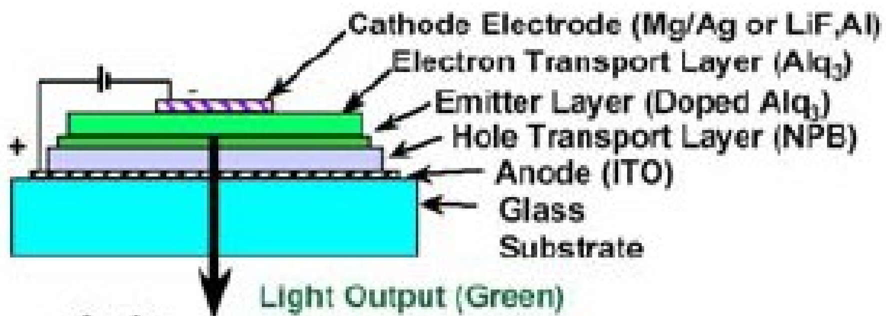
$\eta_{EL}|_{max} = 25\%$

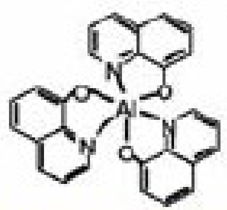

Typ. derivative of Triarylamines
LUMO (conduction band)
electrons
e-
e-
e-
anode
Hole injection
Hole transport
Emissive Layer with dopant
Hole blocker and Electron conductor
cathode
holes
-5.0
~-5.6
"staircase" effect
-6.1
-6.1 to -6.4 required
-6.5
HOMO (valence band)
Doped region (1-2% wt) with organic dye (tuned color)
Typ. derivatives of metal chelates such as Tris(8-hydroxyquinolate)Alluminates (Alq3)

Layered OLED – Small molecules (1990)

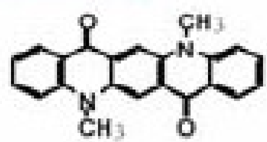
Brevetto Kodak



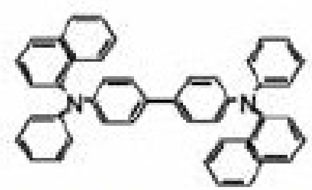




Electron Transport
Layer Material - Alq$_3$



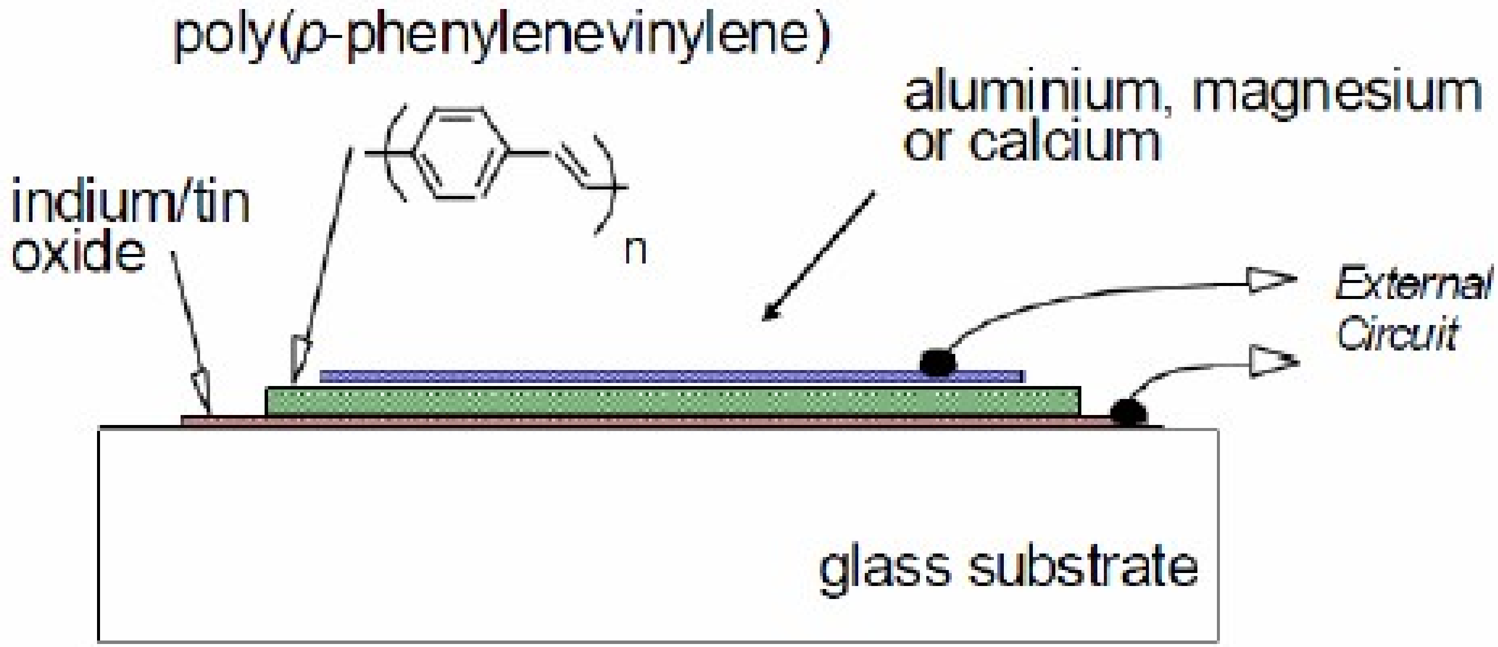
Dopant - DMQA
DiMetil QuinAcridone



Hole Transport
Layer Material - NPB
Naftalene Phenil Benzidina

Thickness of single layers : from 20 to 80 nm

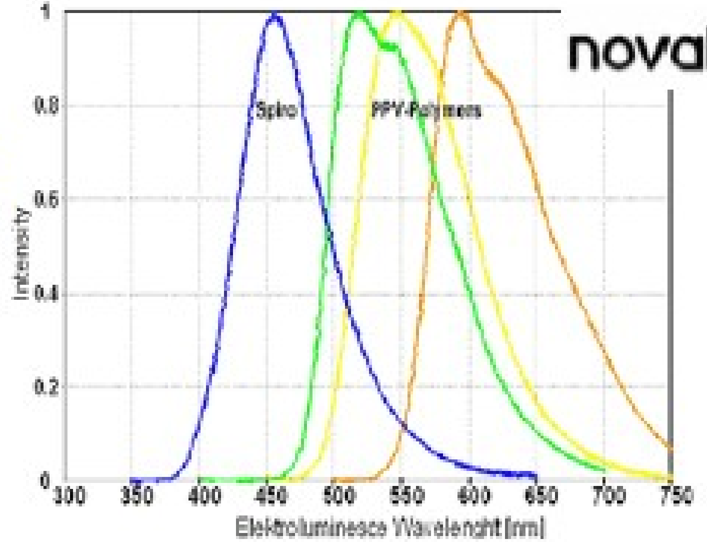
First layered OLED – Polymers

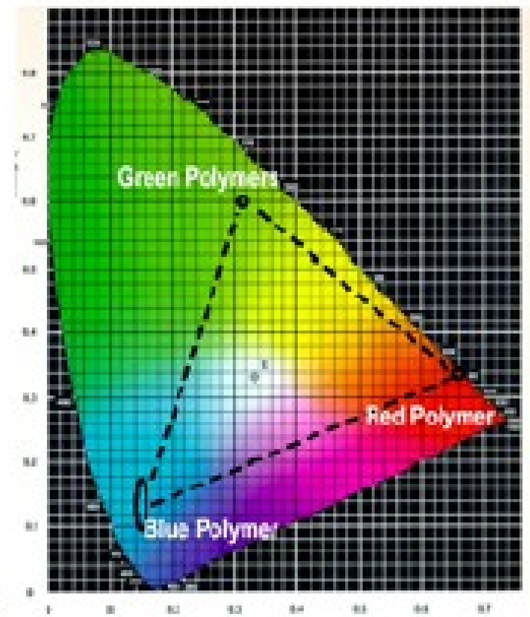


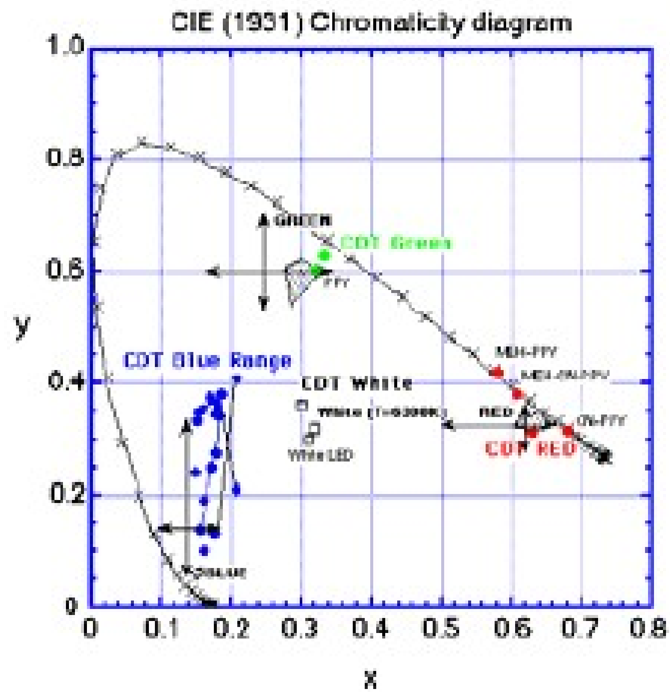
Burroughes et al.

Nature, **347**, 539 (1990), US patent 5,247,190

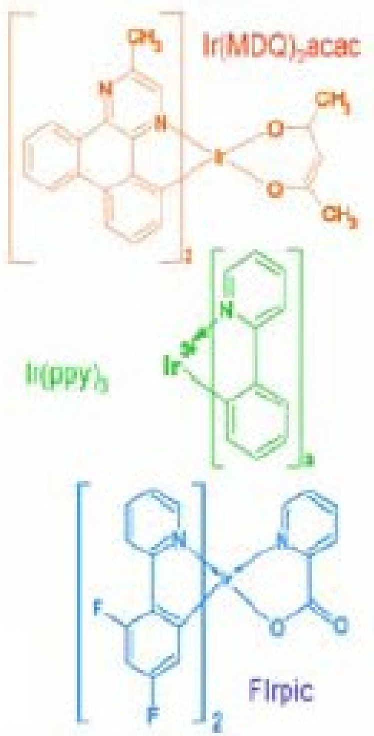
Examples of polymers



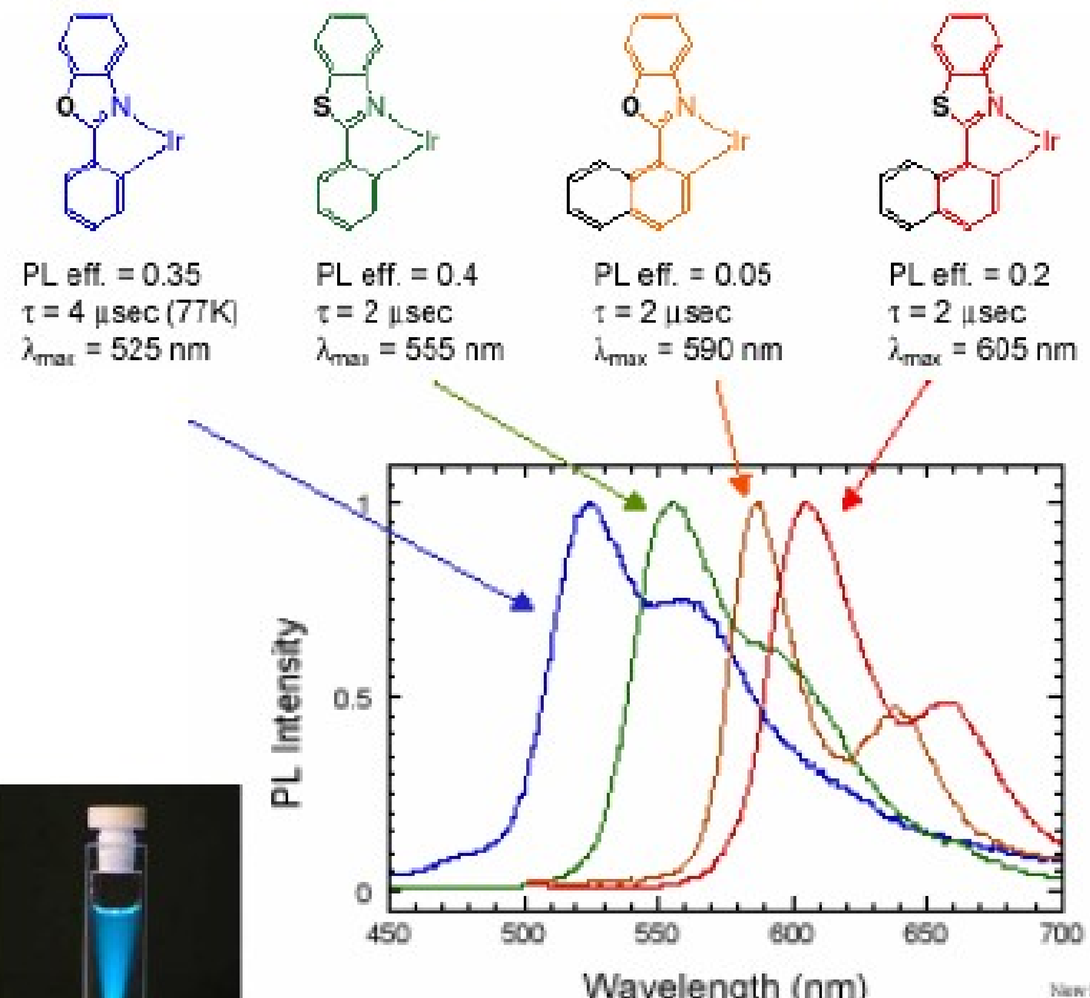


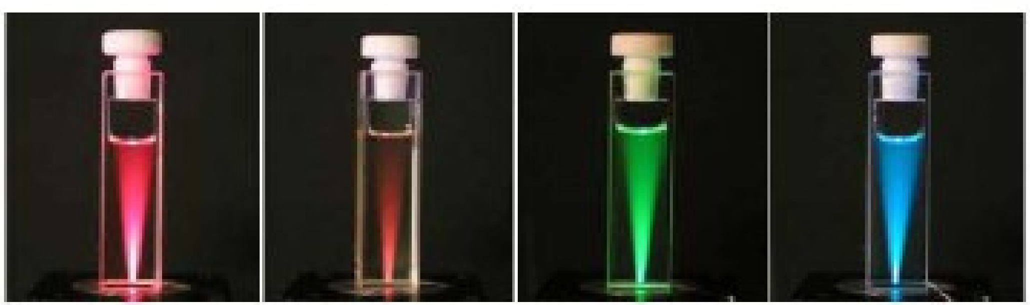


Triplet harvesters : Iridium complexes

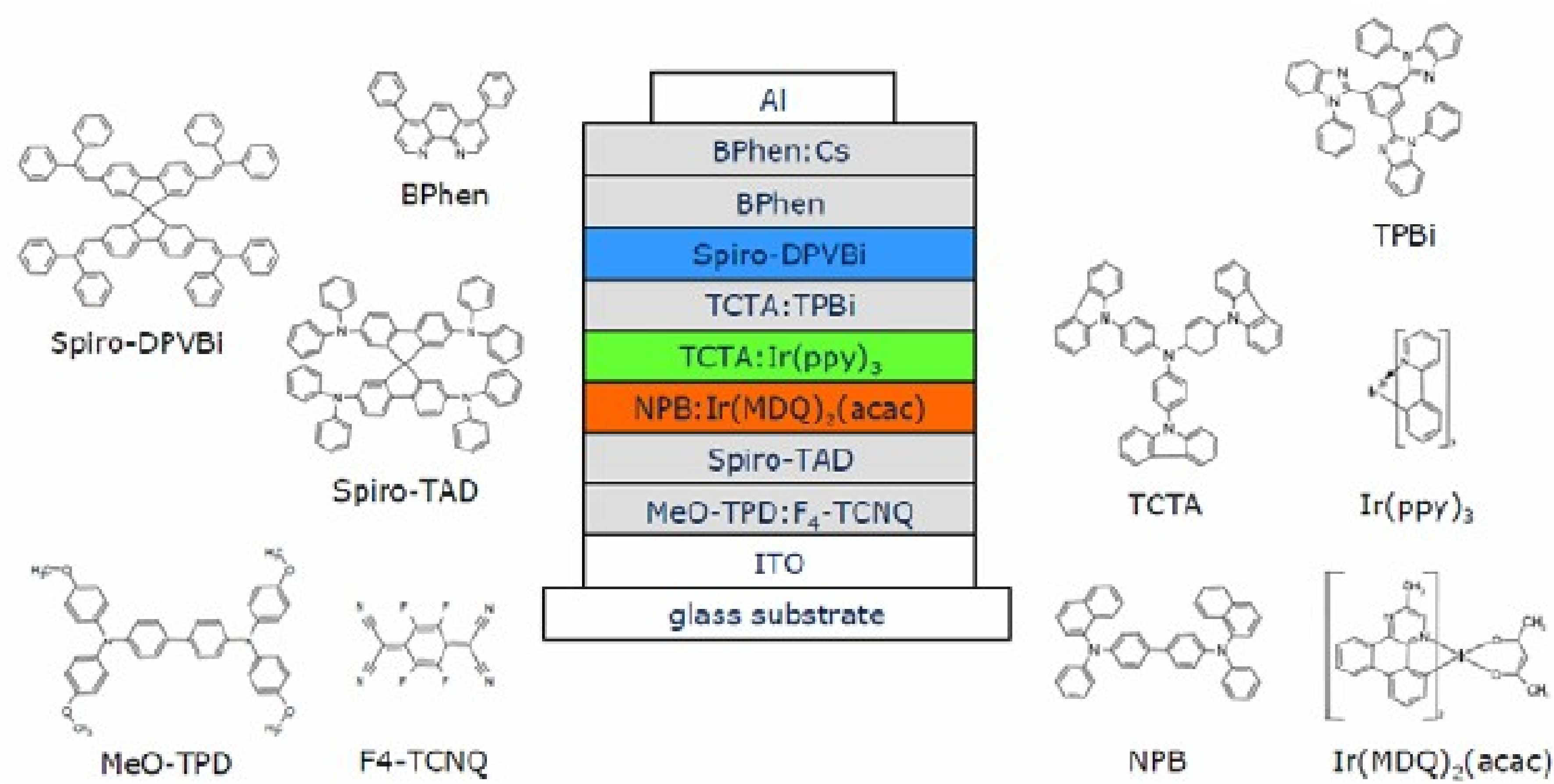


Emitted colour changes by changing the legand :





WHITE OLED – a complex system !



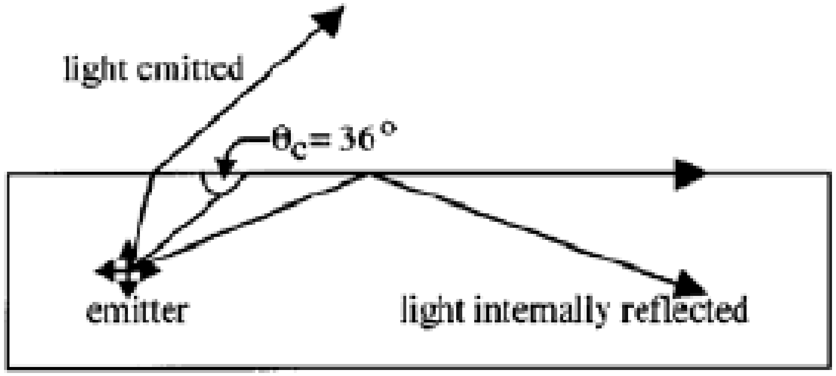
Optical output coupling

$$\eta_{ext} = \gamma \cdot r_{st} \cdot \eta_{PL} \cdot \eta_{coupling}$$

Is related to the extraction of the light toward the external environment

Mismatch between refractive index of EL layer and air → Total reflection for $J > J_c$ (critical angle) → Light is trapped

E.g.: $n_{EL} = 1.7$ → $J_c = 36°$



Simple expressions (from Snell's law)

•If one side is a prefect reflector and the emission is isotropic (molecules):

$$\eta_{coupling} \approx 0.5 / n^2$$

Simplified model, neglecting:

1. **Optical losses**
2. **Interferences**
3. **Absorption at the metal contact**

Typical values :

η = 17% for isotropic emission !!

How to increase $\eta_{coupling}$?

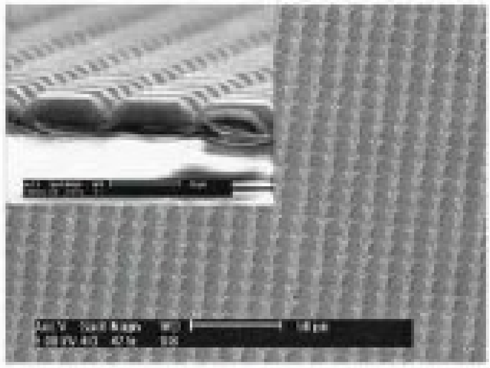
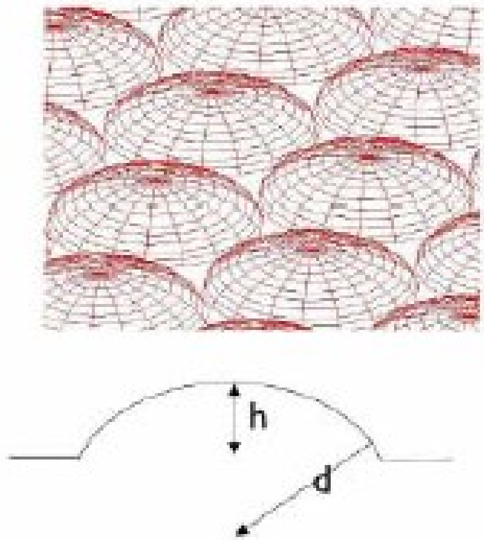
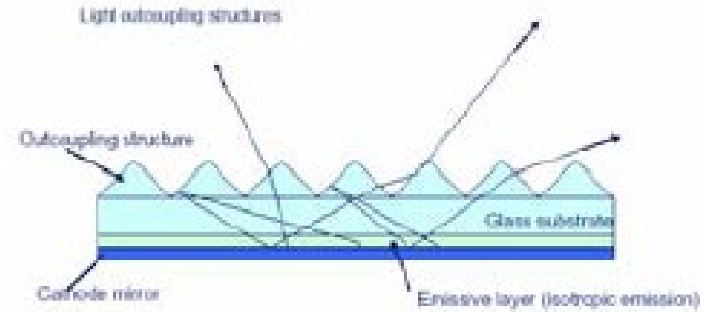
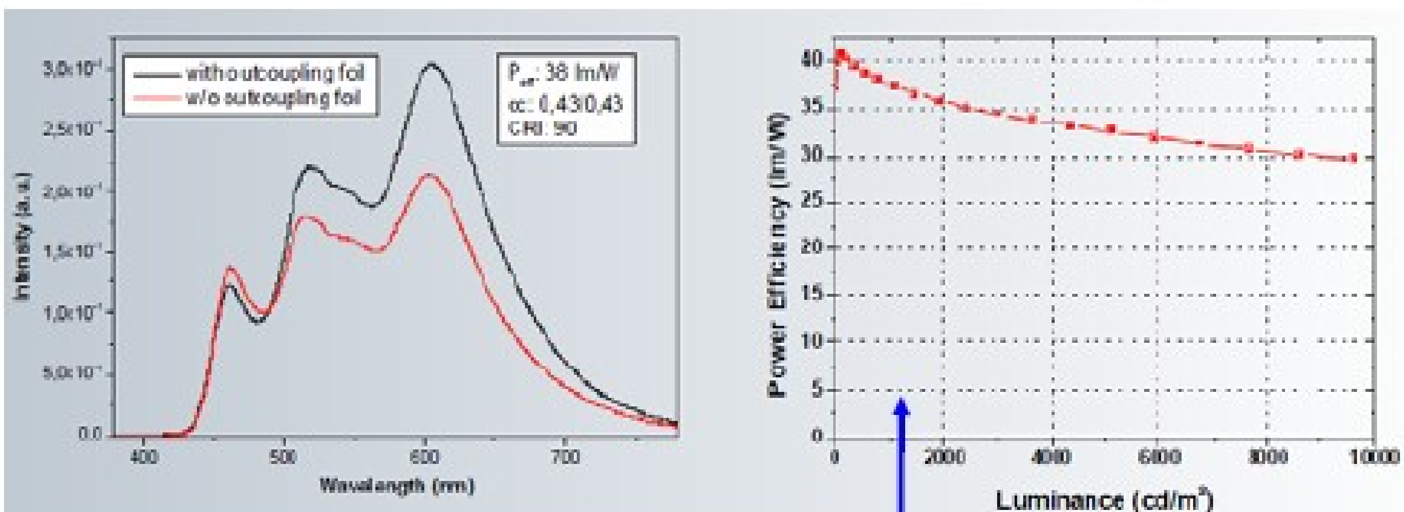


FIG. 3. SEM of a PDMS microlens array fabricated from the mold shown in Fig. 2. The detailed side view of the lenses (inset) shows that the PDMS accurately images the mold shape.





- The outcoupling structures randomize the light ray directions
- Normally, less than 50% of the light entering the glass can escape
- Optimised systems can increase this figure to about 80%



Lifetime : 100.000 h @1000 cd/m^2

Many factors influence OLEDs efficiency

- Charge balance (+ 50 %)
- Singlet-triplet ratio (1:1 for polymers and 1:3 for molecules)
- Non-radiative processes (intrinsic η_{PL}~40%, interaction with metal)
- Output coupling (up to 50 %), lower for small molecule OLEDs

Typical efficiency value for polymer-based OLEDs → $\eta \approx 5\%$ →

- 75 % Charge balance
- 50 % Singlet-triplet
- 40 % Non-radiative losses
- 35 % Output coupling

Factors to improve

- The different factors must be considered together
- Target: η=25 % in the near future
- Use for display applications

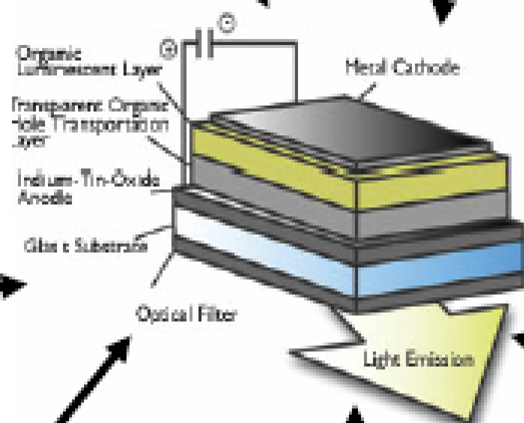
Summary of OLED characteristics

LUMINOSITA' di PICCO
100000 cd/m^2
(400 cd/m^2)

EFFICIENZA
40 lm/W
(2 lm/W)

Lampadina	20 lm/W
CRT TV	1.5 lm/W
LCD display	2 lm/W
OLED	40 lm/W
PolyLED	20 lm/W

ANGOLO
VISIONE
>160°
(60° - 150°)



TUTTI I
COLORI

COSTRUZIONE
A BASSO COSTO

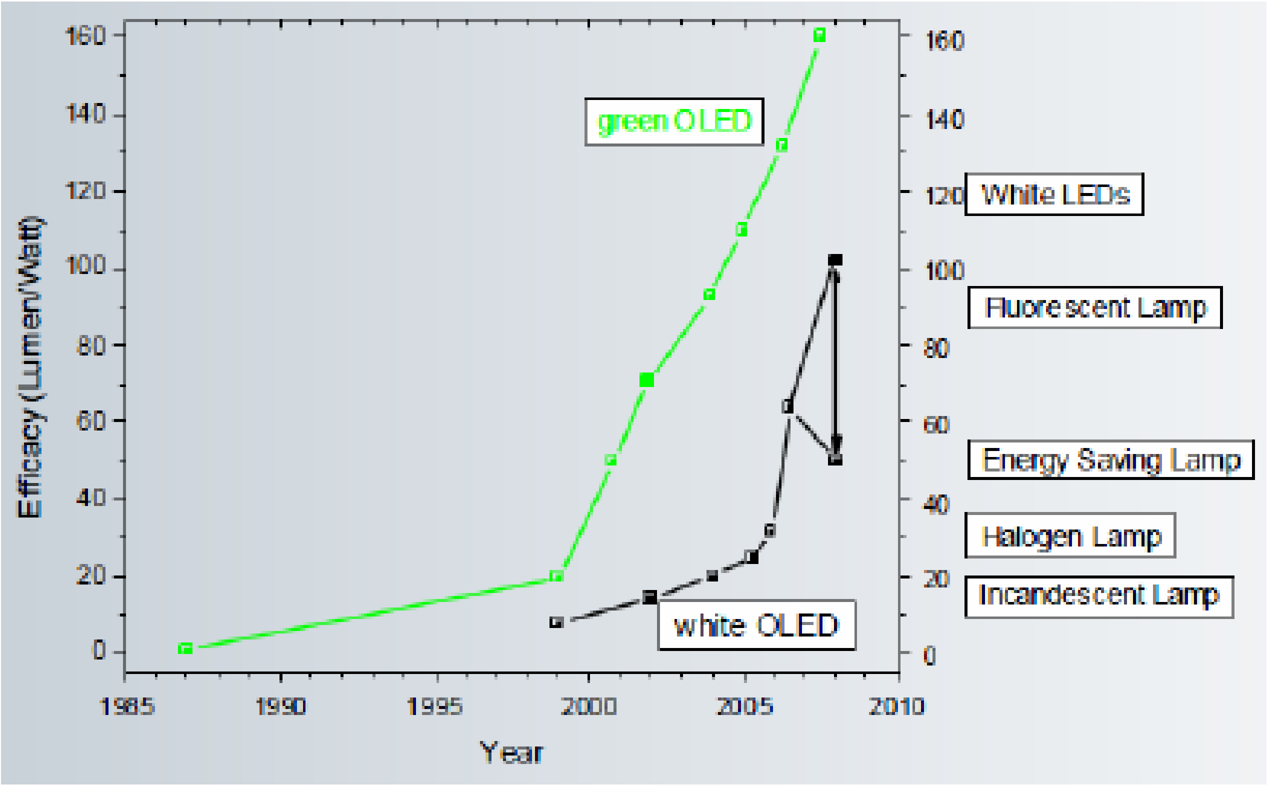
ALIMENTAZIONE
< 10 V
(Backlight!)

TEMPO DI
RISPOSTA
pochi µs
(16 ms)

TEMPERATURA
-80°C / 80°C
(0°C / 40°C)

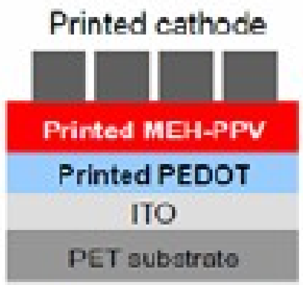
(AMLCD- Langfelder)

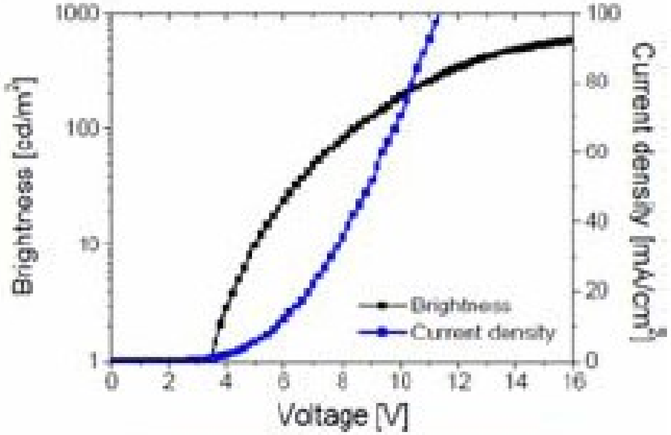
OLED power efficiency development



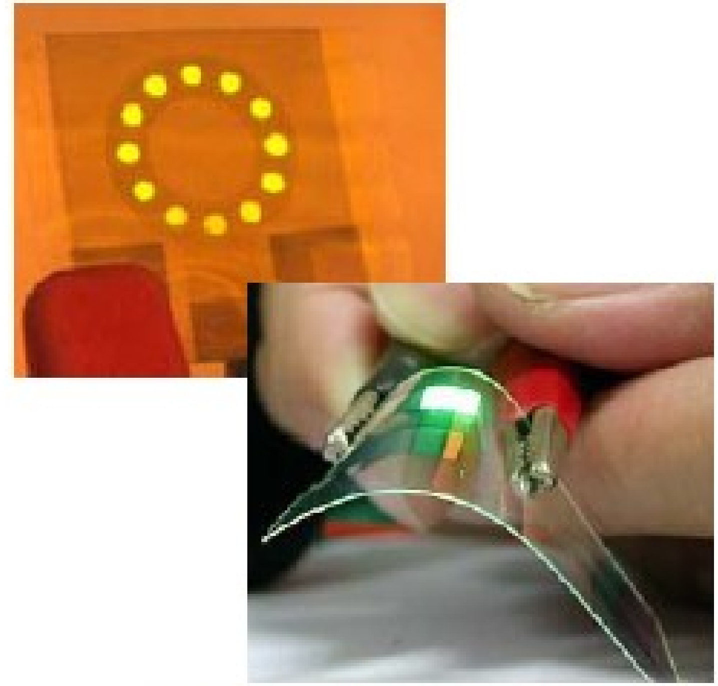
Performance	Status	Potentials
Voltage	3-4 V	2.5-3 V
Internal QE	25-50 %	75-100 %
Outcoupling efficiency	25-50 %	> 50 %

All printed FLEXIBLE oLED

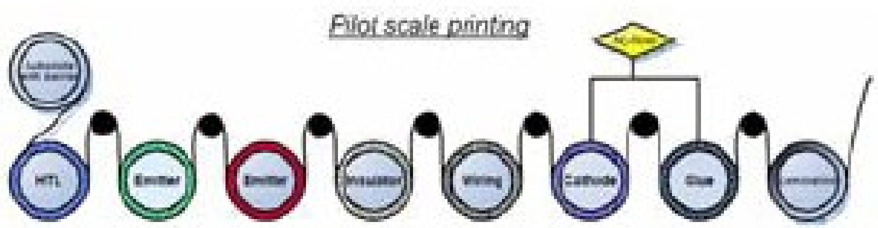




Turn-on voltage	3.4 V
100 cd/m²	8.4 V



Kitamura, *Appl. Phys. Lett.* 83 3410 (2003)
Kitamura, *J. Phys.: Condens. Matter* 20 184011 (2008)



VTT TECHNICAL RESEARCH CENTRE OF FINLAND

AREA source of light - ILLUMINAZIONE

OLED (area source) competes with fluorescent bulbs (line source) and LED (point source)

Grande area attiva
(carta da parati, pannelli luminosi, segnaletica - *luce diffusa, minime ombre*)

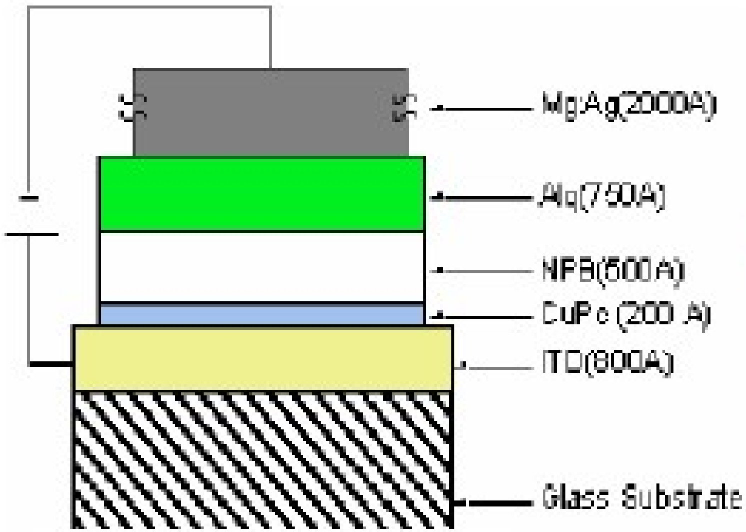
Flessibilità meccanica
(opere curve, adattabilità a forme preesistenti, …)

Infinita scelta di colori
(luci d'ambiente, Color Rendition Index $\rightarrow$100)

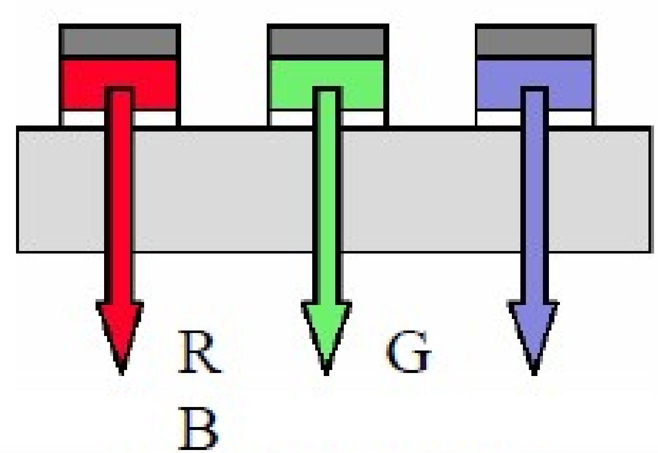
In prospettiva grandi opportunità per designers ed architetti

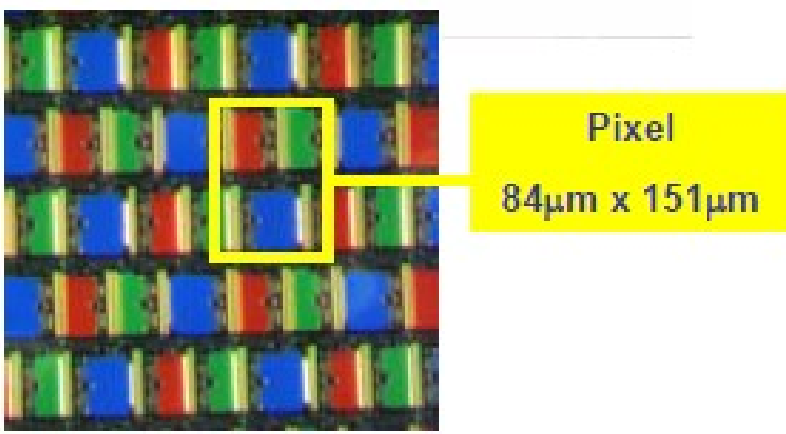
Problemi : disuniformità su grandi aree, tempo di vita, …
… a little electrical short can kill a large area OLED !!!

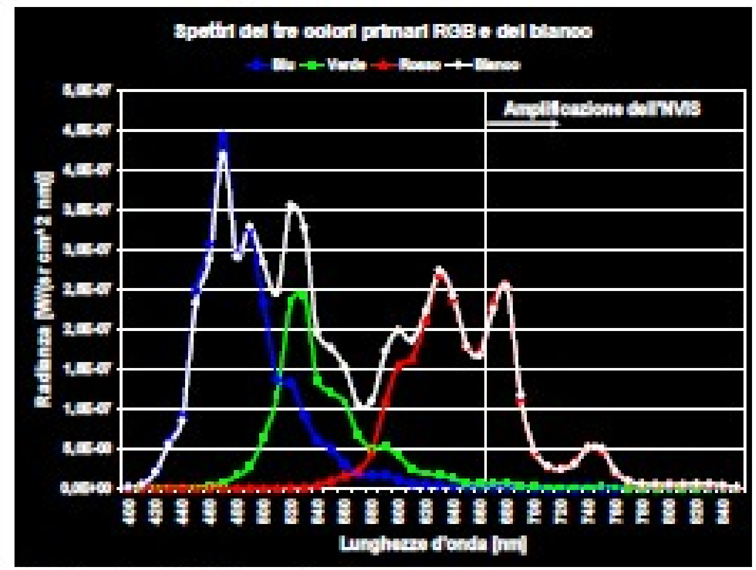
Multi PIXEL - SCHERMI



MOLECOLE SEMPLICI

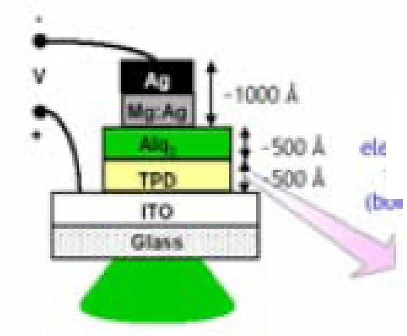






Politecnico di Milano e Logic Spa

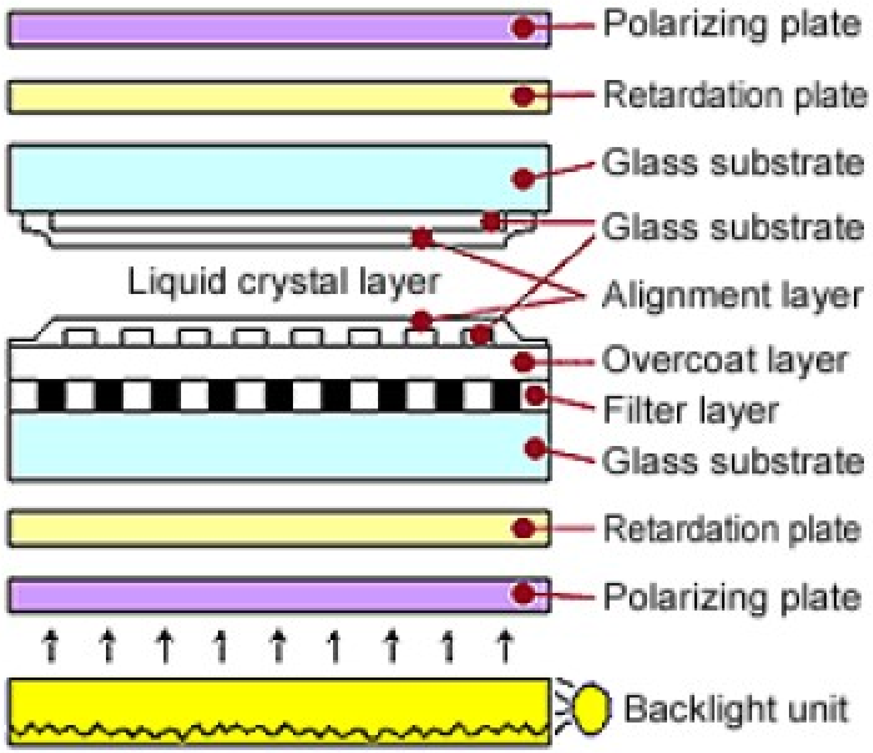
WHY ORGANIC LED Display



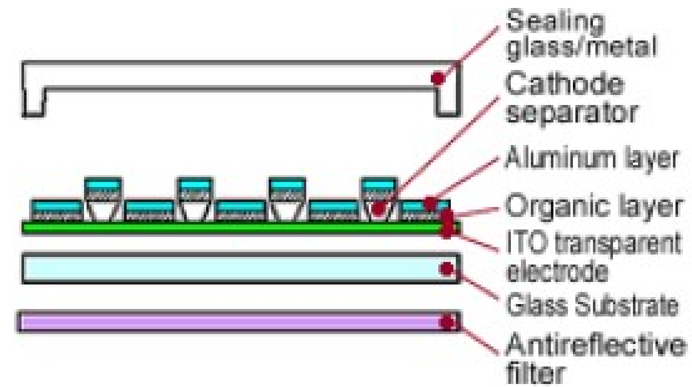
- **Brightness** 100,000 cd/m^2
- **Efficiency** >30 lm/W
- **Low Voltage** from 3 to 10 V
- **Fast** response < µs
- **Low Cost** Deposition Techniques
- **Wide** Viewing Angle >160 deg (Lambertian emission)
- **Scalable** Emissive Area - from a few µm to a few cm
- Colors - fluorescent R,G,B and phosphorescent R,G, covers almost 90% of National television System Committee (NTSC) color spectrum standard
- **High contrast**
- **Good lifetimes** > 10.000 hours
- **Very thin and lightweight**

LCDs vs OLEDs

Light manipulator



Self emitter



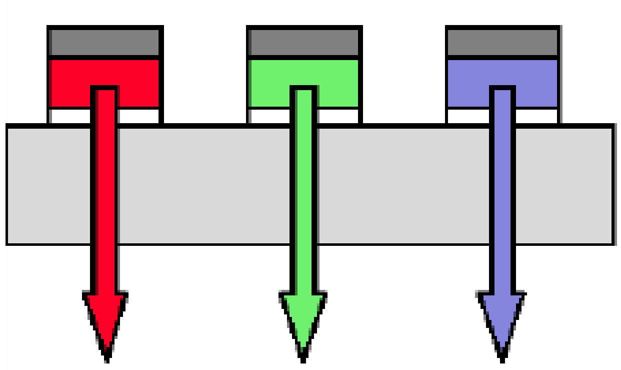
Courtesy Tohoku Pioneer Corp.

OLEDs' advantages over LCDs' are:

1. Simpler structure (thin & lightweight)
2. Better visibility (wide viewing angle)
3. High contrast (when off, it is black !)
4. Faster response
5. Operation at lower temperatures

1 – RGB individual pixels

(Sanyo-Kodak, SNMD)



Il materiale organico emettitore viene applicato separatamente per ogni RGB

ADVANTAGES:

• efficiency (direct vision of emitted light)

• "minori" costi di produzione *(eliminazione dei filtri colorati, ecc.)*

DISADVANTAGES:

• gli emettitori devono essere ottimizzati separatamente

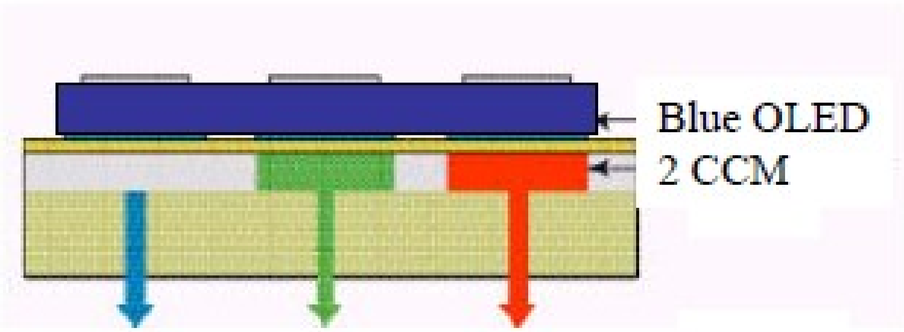
• patterning degli emettitori (polimeri insolubili ?)

• differenti tempi di vita degli emettitori (limited blue lifetime →red shift)

Richiede una tecnologia dell'ITO matura per realizzare litografie più fini

2 – BLUE EMITTER and COLOR CHANGERS

(Fuji Electric)



Only one color of luminescent material

DISADVANTAGES:

• sputtering dell'ITO sui CCM

• necessario emettitore blu stabile

• molte procedure diverse

• Blue emitter must have high efficiency or operated at high current (limited lifetime)

ADVANTAGES:

• no patterning degli emettitori

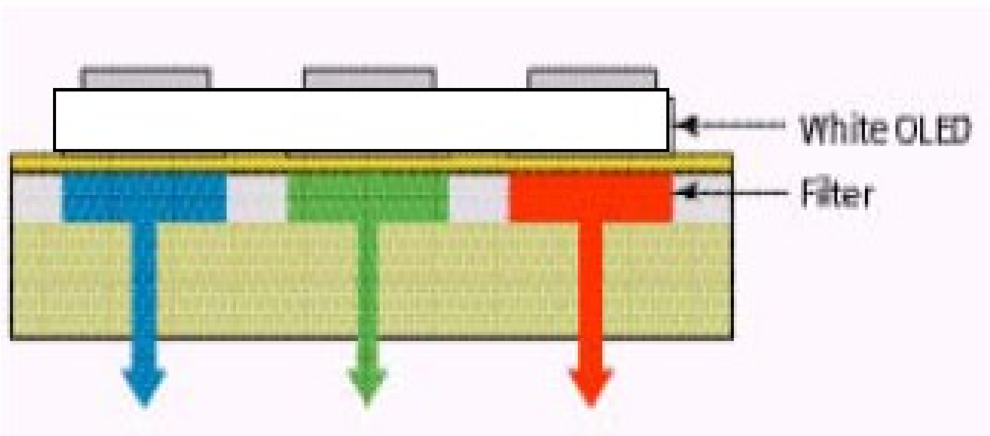
• tempo di vita omogeneo

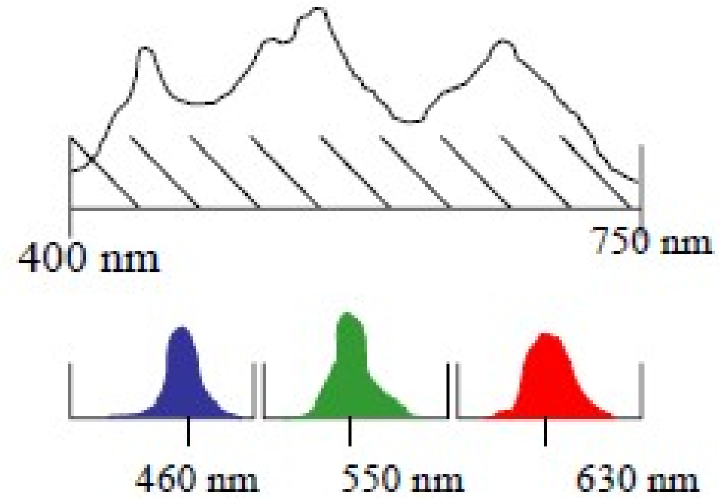
• maggior efficienza rispetto ai filtri

• purezza del colore

3 – WHITE EMITTER and COLOR FILTERS

(Sanyo-Kodak, TDK)





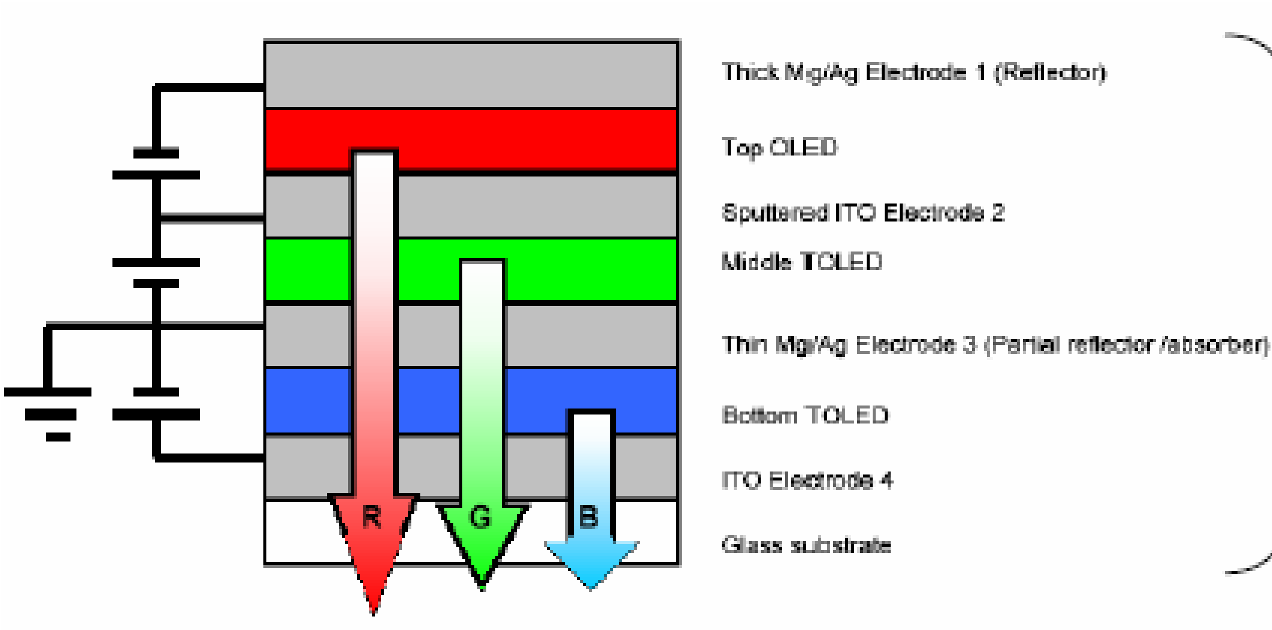
ADVANTAGES:

- tecnologia ben avviata (LCD)
- no patterning degli emettitori
- degrado più omogeneo
- purezza del colore
- area pixel

DISADVANTAGES:

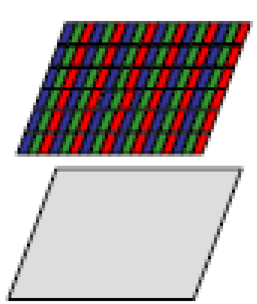
- perdita di efficienza luminosa
- necessario emettitore bianco efficiente e con elevata purezza
- sputtering dell'ITO sui filtri
- calore assorbito

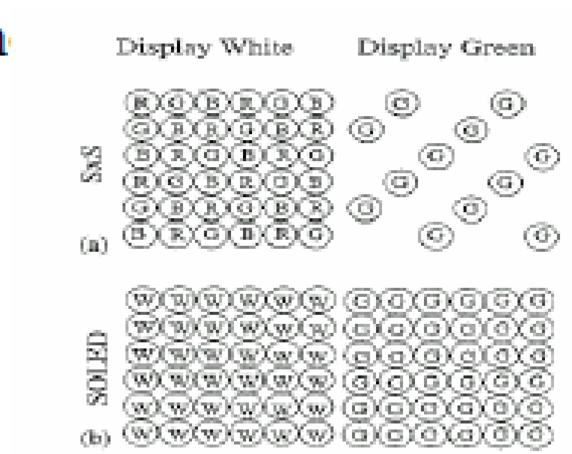
4 – STACKED OLED (SOLED)



(Universal Display Corp.)

- Costruzione più diretta
- No maschere
- OVPD → grande uniformità
- Aumento di risoluzion
- Bianco uniforme

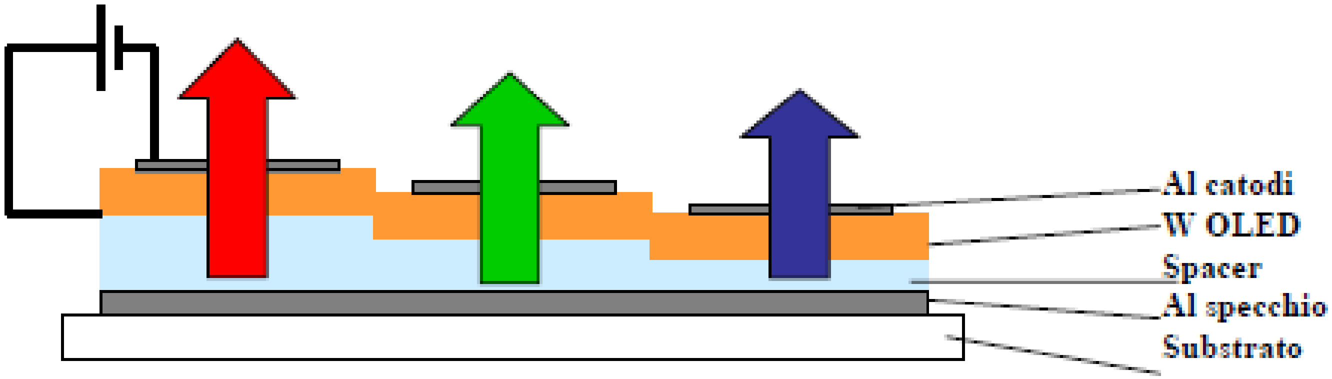




DISADVANTAGES:

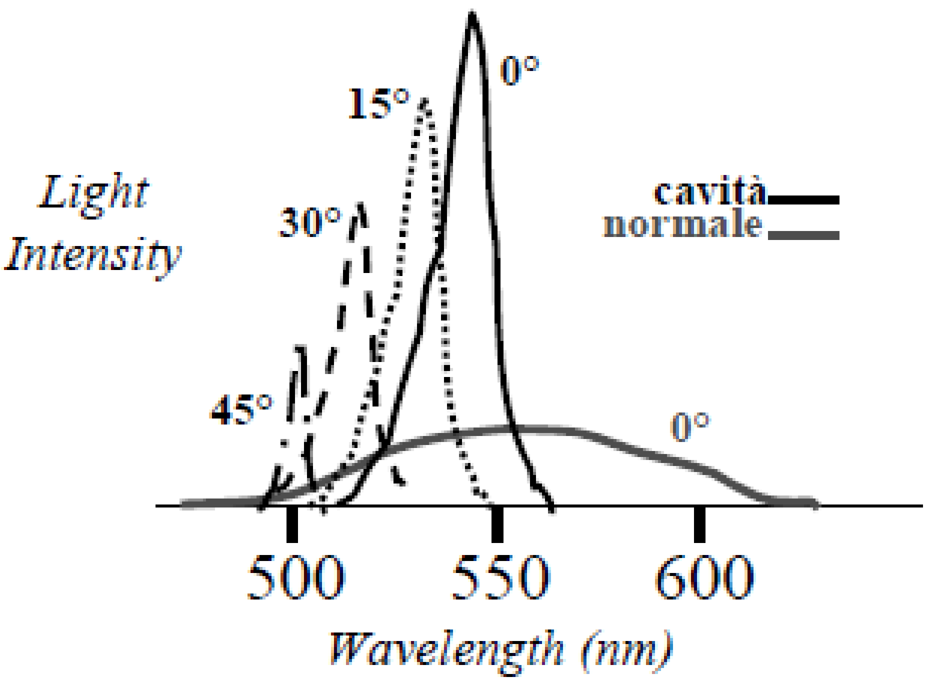
- Complessa struttura multistrato
- No polimeri (difficoltosa deposizione in soluzione)
- Brightness reduction

5 – OPTICAL MICROCAVITY



CONDIZIONE:

$L_i = n^*(\lambda_i/2)$



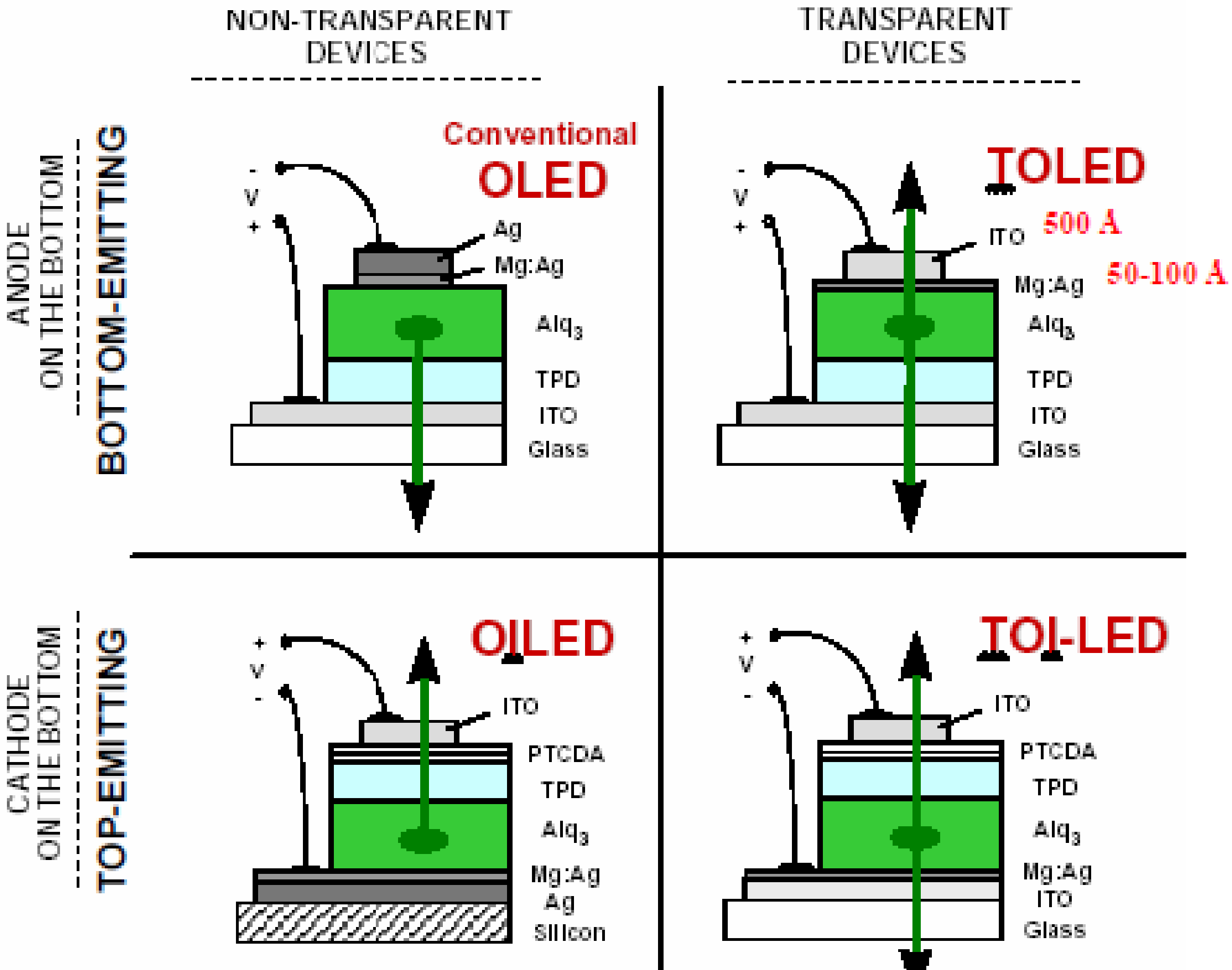
+

- **Amplificazione luminosa**
- **Colori saturi**
- **No patterning, no filtri**

-

- **W.l. shift**
- **Emissione meno isotropa**
- **Costo dello specchio**

TOP or BOTTOM EMISSION



Easier integration with back-plane electronics

Trade-off tra :

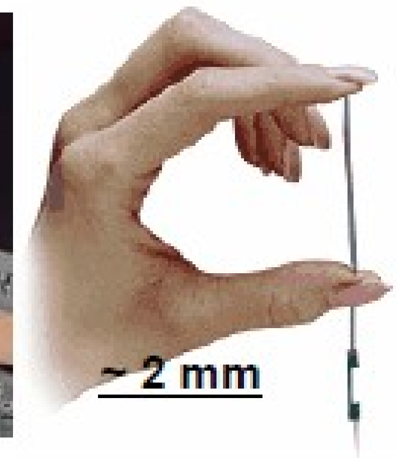
- Trasparenza degli elettrodi
- Conducibilità elettrica
- Funzione lavoro (iniezione)
- TFT shadowing

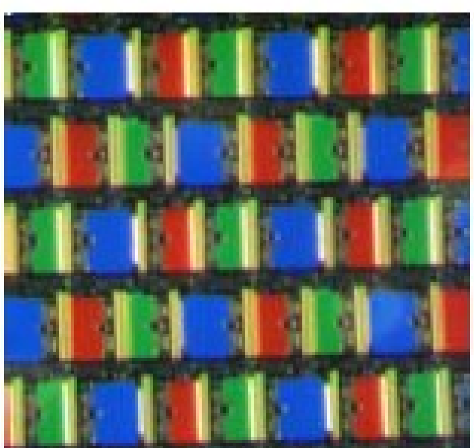
TRASPARENZA >80%
(ANCHE DA SPENTI)

OLED structure influences FET choice (nFET or pFET)

1 - OLED SCREEN : Sanyo-Kodak (1999)

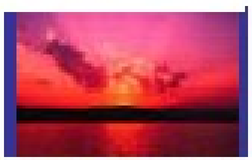
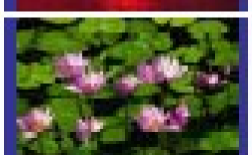
2,16 pollici (5,5 cm)
- Risoluzione: **521 x 218**
- **16,7 milioni di colori** (24 bit)
- Dimensioni pixel: 84 µm x 151 µm
- Temperature di esercizio **-10°C +75°C**
- Tempo di riposta: 10 µs
- Disposizione dei 3 colori: RGB Delta





Fotocamera digitale LS633 di Kodak

Correnti assorbite

Immagine	Corrente OLED [mA]
	0,00
	49,5
	34,23
	39,6
	102,3
	39,8
	16,65

Corrente assorbita dallo schermo OLED dipendente dall’immagine visualizzata

Negli LCD invece la backlight è sempre accesa, quindi il consumo di potenza è costante

2 - OLED SCREEN : Samsung (2009)

3 - OLED TV : Sony (2008)

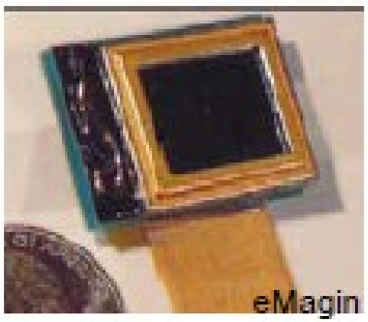
3mm thick !!

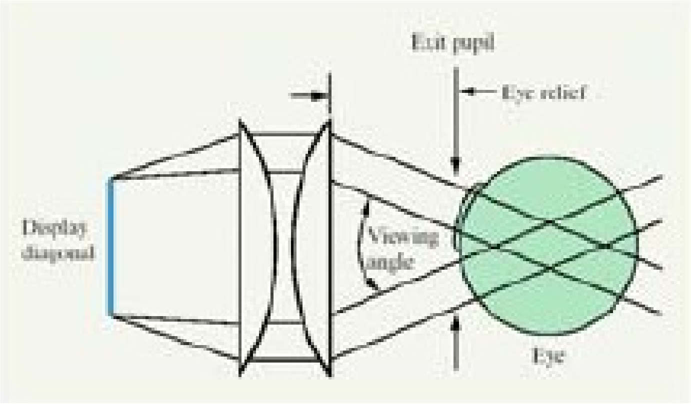
XEL-1 Technical specifications

Pixel resolution	QHD (960H x 540V)
Contrast ratio	1,000,000:1
Panel size (effective picture)	251mm x 141 mm (287 mm diagonal)
Power consumption (stand-by)	45W (0.84W)
Weight	2.0Kg
Lifetime (viewing hours)	30,000 hours (equivalent to 10 years viewing at 8 hours per day)

4 - MicroDisplay

To be viewed near to the eye with *lenses*





- High Resolution and Small Area
  - small size TFT
    - $\mu > 10$ cm2/Vs

make **standard Si** a viable route for substrate

- Careful circuit design:
  A SXGA 1280x1024 with pixel pitch=12μm
  needs a maximum current for pixel of 20nA